Non Equilibrium Thermodynamic Based Transport Studies of Model Membranes



THESIS



Submitted To The Bundelkhand University, Jhansi (U.P.)

For the Degree of Doctor of Philosophy

IN

CHEMISTRY

by

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2006

Dedicated to

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Certificate

This is to certify that the work entitled "Non-Equilibrium Thermodynamic Based Transport Studies of Model Membranes" is a piece of research work done by Mr. Manoj Kumar under my guidance and supervision at the department of chemistry, Bipin Bihari (P.G.) College, Jhansi (U.P.) for the degree of "Doctor of Philosophy" of Bundelkhand University, Jhansi (U.P.) India. He has put in an attendance of more than two hundred days as required by the Bundelkhand University ordinance during the research period.

To the best of my knowledge and belief the thesis:

- (i) embodies the work of the candidate himself,
- (ii) has duly been completed,
- (iii) is up to the standard both in respect of contents and language for being referred to the examinar.

Jhansi: November 2006

(Dr. Mohd. Ayub Ansari)

Declaration

I hereby declare that the thesis entitled "Non-Equilibrium

Thermodynamic based Transport Studies of Model Membranes"

being submitted for the degree of "Doctor of Philosophy" to the

Bundelkhand University, Jhansi, is an innovative piece of work which

has been carried out by me at Membrane Research Laboratory,

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(U.P.)

To the best of my knowledge and belief it has not been submitted

in part or full for any other degree.

Jhansi: November 2006

(Manoi Kumar)

Acknowledgement

It gives me immense pleasure and honour in expressing my deep gratitude and privilege to a person of extra ordinary calibre and versatile genius acts as one's friend, philosopher and guide. I am indeed beholden to **Dr. Mohd. Ayub Ansari, Senior Lecturer, Bipin** Bihari (P.G.) Science College, Jhansi for his ready acceptance to direct the present investigation. It was a gracious gesture on his part to share his valuable time inspite of his busy schedule.

Let it be my privilege to record my hearty gratitude to **Dr. R.S. Kushwaha**, Reader in Chemistry Department, Bipin Bihari (P.G.) Science College, Jhansi for his valuable insight, Priceless suggestions and untiring support through out the course of present investigations.

I would like to express my deepest gratitude and obligation to **Dr. U.P.Singh** Principal, **Dr. S.N. Srivastava** (H.O.D.) of chemistry department and **Dr. Kishore Shrivastave** (H.O.D.) of mathematics department Bipin Bihari (P.G.) college, Jhansi for their utmost co-operation, considerate attitude and constant encouragement.

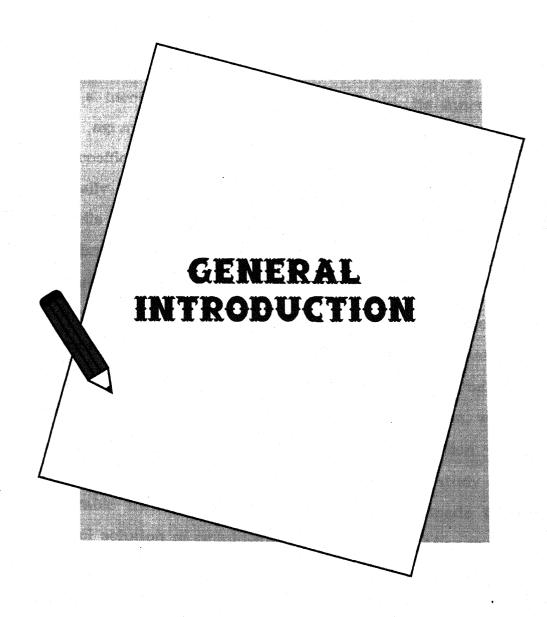
I would like to send very special thanks and heartiest gratitude to **Prof. V.K. Verma**, Director and **Dr. S.D. Sharma**, Resistrar, Sri Rawatpura Sarkar Group of College (SRGOC) Datia, whose modesty, genial and compassionate attitude filled me with inexhaustible energy, hope and elarity to fulfill my goal.

Mr. Firoz Khan and Shahjad Beg (Print Palace, Jhansi) deserve my sincere appreciation for their computer typing and graphics work efficiently in due time.

(Manoj Kumar)

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General Introduction

The word membrane comes from Latin word, "membrana" that means a skin(1). Today's word "membrane" has been extended to describe a thin flexible sheet or film, acting as selective boundary between two phases because of its semi permeable properties. Physically a membrane could be solid or liquid. Its function is a separation agent that very selective based on the difference of diffusivity coefficient, electric current or solubility.

Actually membrane has become an integral part of our daily lives. All cells composing living things, including ours are surrounded with membrane. Biological membranes (membrane cells) are very selective that transfer only particular species.

Model membrane history began in 1748 when French Abble Nollet demonstrated semi permeability for the first time, that animal bladder was more semi-permeable to water than to wine. One century later, Fick published his phenomenological law of diffusion, which we still use today as a first-order description of diffusion through membranes. He was also the first man to prepare and study artificial semi-permeable membranes. The membranes were made from an ether-alcohol solution of cellulose called "collodion". After that many researches were done and many inventions were found such as dialysis, different permeability of gases at rubbeer, osmotic pressure, and Donnan's ion equilibrium phenomena.

Sartorius Werke GmbH, Germany manufactured industrial scale membranes, microfiltration membranes, for the first time in 1950. Before that, membranes were developed in small scale for laboratory applications (2). However, the most fundamental break through in membrane technology came in late 1950s when Loeb and Sourirajan discovered very thin membranes for reverse osmosis, the asymmetric membranes.

Nowadays membrane applications spread over various (metal recovery, pollution control, air enriching for industries combustion). food and biotechnology industries (separation, purification, sterilization and by product recovery), leather and textile industries (sensible heat recovery, pollution control and chemicals recovery). Other industries that also use membrane technology are pulp and paper industries (replacing evaporation process, pollution control, fiber and chemicals recovery), and chemical process industries (organic material separation, gas separation, recovery and recycle chemicals). Medical sector including health-pharmaceutical and medical industries (artificial organs, control release (pharmaceutical), blood fractionation, sterilization and water purification) and waste treatment (separation of salt or other minerals and deionization).

Generally, there are several processes to synthesize membrane, some of them are sintering, stretching, track-etching, phase inversion, and coating. There are several ways to classify membranes. Based on their materials, membranes are classified as polymeric membrane, liquid membrane, solid (ceramics) membrane and ion exchange membrane. Based on their configuration, membranes are classified as flat (sheet) membrane, spiral wound, tubular, and emulsion. Based on what they do any how they perform, membranes are classified as fine filtration (microfiltration/MF,ultrafiltration/UF, nonofiltration/NF, and reverse osmosis/RO), dialysis, electrodialysis (ED), gas separation

(GS), carried-mediated transport, control release, membrane electrode, and pervaporation (PV).

Membrane processes are classified based on various driving forces, some use pressure difference (microfiltration, ultrafiltration, reverse osmosis, and piezodialysis), while others use other driving forces such as concentration difference (gas separation, pervaporation, liquid membrane and dialysis), thermal (membrane distillation, thermo osmosis) and electric (electro dialysis).

The principal advantages of membrane processes compared to other separation processes are low energy consumption, simplicity and environmental friendliness. Membrane-based separation is a result of different rate of transfer between each substance in membrane and not a result of phase equilibrium or mechanically based separation. Therefore, there is no need to add additive material such as extractor and adsorber to proceed the separation. Then we can say that membrane technology is "clean technology", in which no additive materials, which may be potential pollutants are needed.

One of the major advantages of membrane technology is low energy consumption. Membrane based separation is not a result of phase equilibrium that takes a lot of energy to achieve and maintain. It also means that the process could be done in normal conditions where no phase change occurs. Phase change may affect the quality of materials and products. Therefore, membrane technology is suitable for the pharmaceutical, biochemical and food industries.

Designs of membrane module are very simple, compact and easy to use. In addition, not much auxiliary equipment is needed. There is a unique phenomenon in membrane where the scale of process and operating costs are related propertionally. This

phenomenon may be caused by the modular-nature of membrane. This nature distinguishes membrane processes from other processes such as distillation, in which an increase in the process scale is followed by a decrease in cost until economical condition is reached. Not only in cost spent, but also in operating condition. Adding several modules including its auxiliary to existing system can do scaling up membrane processes.

Besides the advantages described above, membrane processes also posses several disadvantages, such as flux optimization and selectivity, material sensitivity, fouling and dependability, Until now there have been several studies conducted to overcome the disadvantages and drawbacks in membrane processes.

Flux and selectivity problems arise as an increase in-flux is usually followed by a decrease in selectivity, while we aim at increasing both. Therefore membrane processes are suitable for very selective separation in which flux is not concerned such as that carried out in pharmaceutical industries.

The dependability problems arise as the characteristics of membrane differ from each other. It is due to the different characteristics of each membrane that a direct scale up of membrane processes is virtually impossible. Before a process is applied in an industrial scale, it is suggested to have a laboratory assessment of the membrane. In this way we may have better prediction on process performance.

Other major problems are material sensitivity and fouling. Polymeric membranes have limited stability (chemically, Physically, and biologically), which restrict the conditions of membrane processes applied. Now a days, there are efforts to invent materials, which may

overcome these constraints. Fouling causes a decline in performance of membrane processes, in which flux (performance of membrane processes, in which flux (performance) is very high initially but then decline drastically as materials of foulant accumulate on membrane surface. Solutions to the problem may lie in the hydrodynamic of the process and pretreatment processes.

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The transport processes occuring across the membranes are of great interest for biologists, who use them as simple models for physiological membrane in order to understand the behaviour of complex cell membranes in terms of established physico-chemical principles. Historically the processes of membrane technology have been defined by various scientists and technologists in different ways which have been revised and described in depth during the later part of 20th century. The importance of membranes in living cells can not be overemphasized. The popular view held by the majority of investigators is that the membranes are a larger part of cell structure. Membranes not only separate the individual cells, but also constitute a part of their internal structure. It is because of this widespread recognition of the membrane nature of cells and the functional role of membranes associated with the living state that an increasing amount of research is being devoted to membrane study.

The use of semi permeable membranes for various separation problems has been of interest of chemists, biochemists and chemical engineers for many years and abundant technical information on the subject has appeared in print. Much of the membrane development work has resulted from the research on conversion of saline water into potable water and water for industrial use by using the reverse osmosis (RO) technique. There has also been a rapid increase in

interest in membranes and related to devices for treating a broad spectrum of industrial effluents having extreme chemical and thermal environments. However, the development of polymeric membranes for diverse applications is still a challenge to polymer and membrane chemists.

The recent progress pertaining to membrane diffusion and transport problems has been achieved in varying fields like chemistry, physiology, pharmacology, biophysics, industrial chemistry etc. in which the starting points and aims have been different. Physicochemical approaches have been made on several biological problems which are well described, but could not be explained satisfactorily. Surface chemistry, solution theory, colloid chemistry, electrochemistry etc, have been employed to solve the biological problems. There are several areas of membrane research which have potentially reaching consequences to medicine and chemical industry. The work in this field is contributing significantly to the economic prosperity and physical well being of all the mankind.

According to physical chemists, the knowledge of transport processes across artificial membranes, if applied in the right direction can solve many secrets of nature. The biologists have recently employed more quantitative methods of research and accumulated enormous data suitable for theoretical studies. Membranes of varying degree of permeability and semi permeability occur universally in plant and animal organisms, constituting there one of the fundamental devices which regulates the exchange of material and thus the flux of life.

Electrochemistry is pertinent in membrane studies according to Buck (3) at three levels. One is the development of techniques with

applications to experimental phenomenology including current-voltage - many items which, may be considered as techniques of analytical separation. Among these are the techniques whose developments and applications belong mainly in the domain of clinical and medical chemistry, physiology, pathology chemical engineering, industrial chemistry, and the various ecological and public health sciences. They are nevertheless capable of practical application and extension in the analytical laboratory.

Transport processes occurring across artificial membranes separating different solution have attracted the attention of chemists, chemical engineers and biologists etc. Chemists and chemical engineers would like to understand the mechanisms of transport so that with the knowledge so gained they would be able to fabricate membranes of any desired property or properties. Biologists, however, would like to use them as simple models for the physiological membranes in order to understand the behavior of complex cell membranes in terms of established physico-chemical principles. The recent progress pertaining to membrane diffusion and transport problems have been achieved in varying fields like Chemistry, Bio chemistry, Physiology, Pharmacology, Biophysics, and Industrial Chemistry etc. in which the starting points and aims have been different. Surface chemistry, Solution theory, Colloid chemistry, Electrochemistry and Thermodynamics etc. have been employed to understand the mechanism of transport in living cells, desalination and electrodics. There are several areas of membrane research which have potentially far-reaching consequences to medicine and chemical industry.

The literature in book form describing membrane technology

and applications is far too extensive to mention. The principal volumes containing significant sections on, or totally devoted to membrane electrochemistry are by Lonsdale (4) clarks and Nachmansohn (5), Helfferich (6) Spiegler (7,8), Merten (9), Marinsky (10), Stein (11), Cole (12), Lakshminarayanaiah (13-15), Hope (16), Arndt and Roper (17), Polensey (18), Kotyk and Janacek (19) and others. Continuing series are edited by Bittar (20), Eisenman (21), Danielli, Rosenberg and Cadenhead (22). Applications of membrane electrochemistry to yield activity sensing electrodes are amply described in books edited by Eisenman (23) and Durst (24). However, this field has produced such a variety of new measuring devices and has opened so many analytical possibilities in terms of new analysis and new detection systems that it is very likely that additional volumes will soon appear. Numerous recent volumes are concerned. in part, with membrane electrochemistry (25-33).

In simple terms membrane (34-36) described as a phase, usually heterogeneous, acting as a barrier to the flow of molecular and ionic species present in the liquids and/or vapors contacting the two surfaces (11). The term heterogeneous has been used to indicate the internal physical structure and external physicochemical performance (37-38). From this point of view, most membranes in general, are to be considered heterogeneous, despite of the fact that, conventionally, membranes prepared *from* coherent gels have been called homogeneous (39).

The notion of homogeneous versus heterogeneous membranes proves to be an important distinction from the point of view of mass transport. In the dilute solution limit, the friction coefficients for mass transport by diffusion or migration are interconvertible by onsager

reciprocal relations and both can be related to jump distances and frequencies according to random walk models. As long there are no preferred regions of low friction in the membrane, it is isotropic on a molecular level and is considered to be homogeneous. Uniformity of mesh on a molecular scale is another view of homogeneity, Channel free solid and liquid membranes are usually homogeneous, and two phase membranes such as solid crystallites imbedded in a non-ionic resin are clearly heterogeneous. The distinction, however, is not always essential (40).

Membranes may be solid liquid or gas (41) and the outer phases are usually liquid or solid. Membranes are usually thin in one dimension relative to the other two dimensions. This property is only functional or operational. In order to achieve a measurable chemical change or electrochemical effect and to make chemical electrochemical measurements on a membrane system in reasonable time, some' transport related property must be susceptible to temporal change. Thus, a change in potential, flux, or concentration (among many varying and measurable quantities) requires membrane thicknesses d such that $d^2/2D$ is comparable with the observation time (D, is a mean diffusion coefficient). Although irregularly shaped membranes are conceivable, most theories and experiments are restricted to systems with one dimensional, or spherical symmetry such that transport occurs in one dimension, the x direction in parallel-face, planar membranes or along a radius in membranes with spherical shape.

Membranes are considered to be porous or nonporous depending upon the extent of solvent penetration (42). At the nonporous extreme, the membranes are nonionic and contain

negligible transportable species at equilibrium. Ceramics, quartz, anthracene crystals, and teflon films between metal electrodes or electrolyte bathing solutions are solid membrane examples. Organic liquid films such as hydrocarbons and fluorocarbons in contact with aqueous electrolyte are liquid membrane example. At the other extreme are porous membranes, which can be solvated and will contain components from the outer phases. Among these are nonionic films such as cellophane, inorganic gels, and loosely compressed powders in contact with aqueous solutions. These materials absorb solvent from the surrounding media and may also extract other neutral molecules and ionic salts. More widely studies are the membranes of polyelectrolytes, aqueous immiscible organic liquid electrolytes (6,13,15,43), various parchment supported inorganic precipitates (42-56), solid ion conducting electrolytes including silver halides, rare earth fluorides, and alkali silicate and alumino-silicate glasses (23,24,57,58,59,60). All these materials contain ionic or ionizable group within the membranes which are capable the property under diffusion or electric field forces in addition to diffusive or electric field forces. In addition these materials also possess the property of porosity. Polyelectrolytes tend to swell rapidly by osmotic pressure driven uptake of solvent. Liquid ion exchangers are surprisingly slow to take up water, while the inorganic salts have not tendency to hydrates. Glass membranes are complicated by simultaneous hydrolysis of the polyelectrolyte during uptake of water (61-63).

Depending on the dielectric constant and solvent penetration, sites are potentially, partially or even completely ionized. A Characteristic of electrolyte membranes is the presence of charged

sites (64-66). If ionic groups are fix in a membrane as SO_3^- and COO^- attached to cation exchange resins, the membrane is considered to possess fixed sites, even if protons or metal ions are covalently bonded to the sites. In glasses, the fixed sites are -SiO $^-$ and -AlO $^-$ groups, while in anion exchange resin membrane, these are - N^+ . On the other hand liquid ion exchangers which are water immiscible such as diesters of phosphoric acid can be viewed as mobile site membranes. The acid is trapped in the organic phase, while the protons and/or other cations can move in and out of the membrane, the phosphonate cannot. Membranes without ionizable groups contain no charge sites. It is important to know that cellulose triacetate, which is initially site free, soon develops negative sites by hydrolysis and oxidation on exposure to aqueous solutions.

The frequent use of "Charged" and "Uncharged" in the membrane literature is usually unsound electrostatically, but does provide an intutive chemical description. For example, "Charged" membranes usually refer to electrolyte membranes such as solid and liquid ion exchangers where the fixed and mobile sites are the "Charges". Actually, these membranes are quasi-electroneutrality in their bulk when the thickness is large compared with the Debye thicknesses at each interface. Quasi-electroneutrality means that in any volume element large compared with the distance between ions, the sum of ionic charges $\sum Z_i C_i = 0$. In the literature, "uncharged" membranes are those, like cellophane, with no fixed charges. This frequently used literature definition provides no place for lipid bilayer membranes, which are electrostatically neutral only in the absence of charge carriers and in the absence of bathing solution whose salts

possess prefrential solubility of anion over reaction or vice versa, but are usually electrostatically charged by an excess of ions of one sign in normal operation. Thick hydrocarbon membranes and membranes of diphenyl ether (or derivatives), phthalate, and sebacate esters are generally neutral in the presence of most bathing electrolytes, but may be charged electrostatically, depending on thickness, in the presence of neutral carrier species which preferentially solubilize ions of one sign. The use of "Charged" and "Uncharged" to describe electrolyte or non-electrolyte membranes has been discouraged unless the precise electrostatic connotation is involved (40).

Membranes may be broadly classified into natural and artificial. Natural membranes are classified to possess a fundamental unit membrane structure which is a bimolecular leaflet of lipid with their polar groups oriented towards the two aqueous phases of the cell, and protein is supposed to exist close to the polar heads of the leaflet. This type of the universal structure is absent in artificial membranes. Eisenman et al. (67) have given a classification of these membrane based on their structures.

Unlike the classification based on membranes structure, membranes are usually classified either on the basis of their nature, i.e., coherent gel or otherwise, or on the nature of the chemical reaction involved in their formation, i.e., addition or condensation reaction. The efforts of various workers have been directed towards:

(A) Preparing membranes with good chemical and mechanical stability and favourable electrical performance suitable for fundamental transport studies and for applications in some industrial operations such as the treatment of brakish water, saline water conversion, etc.,

(B) building suitable models to mimic the properties of natural

membranes, and (C) preparing composite membranes containing cationic and anionic groups in suitable arrangement to demostrate and to study the physicochemical phenomena associated with the rectification of alternating current and other special membranes for specific purposes. It is worthwhile to mention that most of the work concerning category (A) seems to be directed towards finding suitable membrane materials for fabricating a structure for effective desalting sea water by application of pressure. The most commonly used material for casting a membrane for desalination is cellulose acetate although, polymethacrylic acid (PMA), phenoleulfonic acid (PSA), polystyrene sulfuric acid (PSSA) and cellulose esters have proved very useful (68). A number of investigators in recent years have prepared membranes from cellulose acetate under varying conditions and used them to understand the mechanism of water flow (7,8,9,69-83). In category (B) bilayer membranes, first generated by Mueller (84), have most widely been used as model for living cells and the studies have given somewhat a better understanding of the structure and function of the natural membranes. The membranes of catagory (C) are quite numerous (14,40,85-87).

Theories on the transport of charged or uncharged particles across the membranes can be roughly divided according to schlogl (88) into the following groups.

Group one considers the membrane as a surface of discontinuity setting up different resistances to the passages of the various molecular or ionic species (89-90). The driving forces are the differences of the general chemical potential (i.e. differences of pressure of electrical chemical potential included in the general chemical potential) between the two outer media.

Group two considers the membrane as a quasihomogeneous intermediate phase of finite thickness in which the local gradients of the general chemical potential act as driving forces (64,65,91-97) Convection may also contributes to particles transport withing the membrane.

Group three considers the membrane as a series of potential energy barriers lying one behind the other, thus forming, in contrast to group two, an inhomogeneous intermediate phase (98-100). An (irregular) spatial lattice is formed due to the higher probability of finding a particles in the positions between the activation thresholds. The driving forces arise from the differences between the transition probabilities in opposite directions perpendicular to the membranes.

This grouping attempts to classify the various mathematical approaches, according to the ideal models on which they are based. It is in fact too schematic, as many theories occupy intermediate positions. No author is likely to take the view that one of these treatments is right and the others wrong. The various descriptions supplement each other and depending on the system under consideration, one of the three will prove the most suitable. It may be shown, for example, that when the number of activation thresholds becomes very large and the distance between the lattice points sufficiently small, then groups 3 and 2 merge into each other. A transition is also found between group 1 and 2 (88).

Unlike group 3, groups 1 and 2 can be classified in the general scheme of irreversible thermodynamics. In group 1 as well as in group 2, linear relationships are assumed between the particle fluxes and the driving forces. Owing to the differing characters of the driving forces, group 1 is treated according to the method of "discontinuous

system", and group 2 according to that of "continuous systems". An integration in group 2 across the membrane does not as a rule yield a linear relationship between the flux and the general chemical potential difference. Only for sufficiently small differences group 2 merges into group 1 after integration. In this sense group 2 is more general than group 1. Group 2 is, however, inferior to group 1 in that a number of idealizatons must be assumed before an explicit integration can be affected. Kirkwood (101) finds a correction between group 1 and 2. His initial flux equation differs from that normally used in the treatment of "continuous systems" in irreversible thermodynamics. This treatment of Kirkwood has been developed and modified by Schlogl (88). On a broad basis, it may be said that the theories of group 1 are based on the ideas of classical thermodynamics or quasi-thermodynamics which is Restricted to isothermal systems. The theories of group 2, apart from being more regorous and realistic allow a better description and understanding of transport phenomena in membranes and are useful in dealing with non-isothermal systems. The theories of group 3 provides a general and unified view applicable to systems of differing degrees of complexity. Many of the theories based on the Nernst-Plank flux equation are placed in the first groups whereas those dealing with the principles of irreversible thermodynamics and the theory of absolute reaction rates are placed in the 2nd and 3rd groups respectively.

The theories of the first groups have the advantage of being relatively simple. For ion-exchange membranes, however, they are often inadequate. These theories deal chiefly with processes occuring within the membrane. For such a purpose the theories of the second group are proper choice.

The most important theories of the second group are based either on quasi-thermodynamics or on thermodynamics of irreversible processes. The fundamental difference between these two approaches are summarised below.

Quasi-thermodynamics is not interested in particle fluxes. One might say that the quasi-thermodynamic approach consists in taking a snapshot of the system and calculating the emf from the charges which a reversible electric current would produce in the system if it were "frozen" in the state in which the photographic picture was taken. This procedure gives directly the emf of the cell. No model is needed. Taking the snapshot, however, is often not as simple as it may seen. A rigorous treatment would require the knowledge of the composition of every differential layer of the diffusion zone (i.e., the concentration profiles of all species). Since obtaining this information experimentally is usually too lengthy a task or even quite impossible, the quasi-thermodynamic treatment is forced to make assumption about the condition of the system.

The thermodynamics of irreversible processes (102) in contrast to quasi-thermodynamics, does not require prior knowledge of the concentration profiles. The set of equations of thermodynamics of irreversible processes interrelates all occuring "fluxes" (gradients of chemical potential, electric potential, temperature etc.). From measurements of a sufficient number of "phenomenonlogical coefficients", all fluxes and forces and hence also the emf can be calculated, without knowledge of the profiles and without using the concept of "reversible energy production" which on based. Furthermore, thermodynamics thermodynamics is irreversible processes is applicable also to non isothermal systems and includes coupling of fluxes which is not covered by quasithermodynamics. It may be mentioned here that the discipline of irreversible thermodynamics provides a precise mathematical description of the processes of transport and diffusion in membrane system. Its application to membrane processes is a natural development of the basic theory of katchaslky (102) and has been developed by onsagar (103), Kedem (104), Caplan (105), Mears (106), Rastogi (107), Kushwaha (108-109) and others (110-113) in an extensive and expanding literature.

The theory of absolute reaction rate has been applied to diffusion processes in membranes by several investigators. A. Yamauchi, M. Shinozaki, Y. Shine and M. Kawabe (100) considered the diffusion process as one of the basic phenomena for sustaining the growth and development of plants and organism. They presented a detailed kinetic approach to diffusion which clarifies much established concepts and provide impetus to a fresh approach to the problems in the field of biological diffusion. The absolute reaction rates theory treatment of diffusion and membrane permeability provides a general unified point of view applicable to systems of varying degrees of complexity. It is equally adoptable to the treatment of the permeabilities of membranes to electrolytes, from non electrolytes under the driving forces of a concentration gradient, activity gradient, and external and internal potential gradients. A. Yamauchi, M. Shinozaki, Y. Shine and M. Kawabe (100) treatise on membrane diffusion is based on the "activated state" or the "transition state" theory.

Kuniaki Takata (99) have also treated the kinetics of membrane transport under steady state conditions. They employed similar

principles and expressed the rate constant of the over all process of surface penetration in terms of a number of specific rate constants. Various special cases are considered and discussed with reference to the experimental data. They developed flux equations for solvent and solute especially as a function of the osmotic and hydrostatic pressures across the mebrane. Recently, Tien and Ting (114) have applied the theory of absolute reaction rates to diffusion processes through Bilayer Lipid Membranes (BLM) and have derived various thermodynamic parameter like free energy of activation, enthalpy of activation and entropy of activation etc. Weidemann et al. (115) projected about transport properties of vanadium ions in cation exchange membranes and determined the diffusion coefficients using a dialysis cell. Besides of these studies, it was also established that solution diffusion model can be used to describe the ion exchange fluxes. In doing so the flux in a first approximation is given as the product of the solubility and the diffusion coefficient of the exchanging ion in the membrane material the more important factors in membrane transport were mainly the charge densities and pore sizes in membranes (116-118). If these two factors may be controlled appropriate by a better understanding regarding the membrane phenomena such as ion transport or ion selectivity will be enhanced. Transport studies across the membranes not only contribute in basic sciences but also equally in medical sciences. As the effects of high pressure on glucose transport in the human (117, 119) is one of the useful studies. The effects of raised hydrotri pressure on D- glucose exit from human red cells at 25°C were studied using light scattering measurements in a sealed pressurized spectre fluorimeter eurette. The reduction in the rates of the glucose exit with raised pressure provides an index of the activation volume. The activation volume is defined as the difference in partial molar volume between the activated state and the ,reactants of a process.

Application of electrochemistry in membrane studies is pertinent at three levels. One is the development of techniques with application to experimental phenomenology including current-voltagetime-concentration behavior. A second is the mathematical modeling implied by experiment and tested against experiment. The third level is experimental verification of models in terms of the molecular processes and properties and includes determination of theoretical parameters by electrical methods and by complementary none electrochemical methods like: Physical, optical, ESR, NMR, Raman, fluorescence, T-jump techniques, etc. From transition and steady state measurement of current or membrane potential as a function of chemical composition, chemical treatment, and temperature, the roles of kinetic and equilibrium parameters can be deduced or inferred. A possible approach to modeling beings with the assumption of the membrane as a linear system to which laws of network theory may be applied. Another beings by solution of basic electro diffusion laws of transport with equilibrium or kinetic boundary conditions in order to deduce forms for system functions which satisfy the data.

The most important contribution of electro chemists to membrane electrochemistry is the transfer of perspective and wisdom to the new area. There are many sine qua nons in electrochemistry which have occurred through extensive studies of electrolytes and electrolyte/membrane interfaces. Electrochemists have learned to subdivide systems into interfacial and bulk processes and to expect effects of dielectric constant (complex formation, ion pairing), effects of

short range forces (adsorption of charged and, uncharged species with, possibly, changes in rates of interfacial processes), effects of high fields near surfaces (Wien Effect, and dielectric saturation, for example), and the important effect of local potentials on rates of interfacial processes (irreversible charge transfers, psi effects, etc.). In as much as the presence of the space charge at interfaces is a natural consequence of the continuity of potential from one phase to another, the presence of space charge and space charge mediated effects in membrane systems is anticipated.

In this thesis studies of transport properties of polystyrene based inorganic precipitate membranes when they are used to separate various aqueous electrolyte solutions are reported. The membrane electrolyte system has been considered to contain four chemical species, counter-ions 1, coion 2, water 3 and fourth the membrane matrix which carries fixed ionogenic groups and excludes the possibility of chemical reaction within the membrane. The membrane matrix has, therefore, been considered to consist of fixed charge and adjacent polymer segments which together constitute the repeat unit of the matrix. It is, therefore, possible that kinetic coupling interaction of membrane matrix will include not only the contribution of fixed charge, but also specific polymer effects if such exist. This is an important qualification to the description of the species as simple as ion, although it .appears from earlier studies that such effects are small (107, 114-117). The discussion has mainly been restricted to commenting on only a few points concerning the following ionic processes in the membrane systems, "Permeability phenomena".

- 1- Ionic transport "flux"
- 2- Membrane potential

- 3- Electrical conductivity
- 4- Ionic distribution equilibria
- 5- Spatial distribution of ions and the potential within the membrane.

Transport studies across, the inorganic organic composite membrane, ion exchange membrane, and biological membrane based on non-equilibrium thermodynamics have been carried out by various investigators. The most direct theoretical approach to transport phenomena, yukiomizutani (120) reviewed the structure of ion exchange membranes and their studies regarding to membrane properties have also been reported. Electrokinetic effects arise due to the interaction between the flow of matter and flow of electricity through membrane, porous media, capillaries etc. thermodynamics of irreversible processes (121-123) to treat the transport phenomena.

The thesis has been prescribed under the following heads.

1. Membrane Surface Charge Studies:

This portion deals with the measurements of membrane potential across polystyrene based nickel and cobalt phosphate membranes using various 1:1 electrolytes at different concentrations under isothermal condition for the evaluation of thermodynamically effective fixed charge density of the membranes as well as to examine the validity of the recently developed theories for membrane potential including those based on the thermodynamics of irreversible processes.

2. Studies of Metal Ions Selectivity:

This portion deals with the evaluation of membrane selectivity of polystyrene based nickel and cobalt phosphate membranes towards the metal ions from bi-ionic and multi-ionic potential measurements for various 1:1 electrolyte systems. The experimentally observed values of membrane conductance for the same electrolyte systems are also actively involved to establish the selectivity order of ions in the membrane phase.

3. Membrane Diffusion Studies:

This portion deals with the evaluation of diffusion rate of 1:1, 2:1 and 3:1 electrolyte throught polystyrene based Nickel and Cobalt phosphate membrane at different temperatures. Diffusion coefficient and various thermodynamics parameter have been evaluated in order to understand the mechanism of ion permeation through the membranes.

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CHAPTER-I MEMBRANE SURFACE CHARGE STUDIES

Membrane Surface Charge Studies

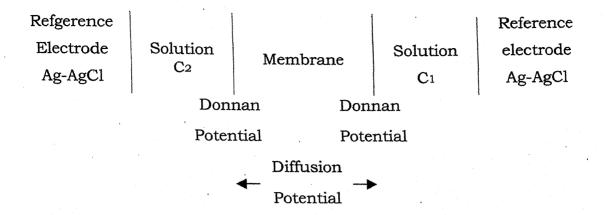
Introduction

Inorganic precipitate membranes because of their stability in various environmental situations have quite often been utilized as a model for the studies of transport phenomena. One of the most consistent properties of biological system is the presence of a voltage across the cellular surfaces. The mechanism where by this potential arises is still in dispute. Some consider it to be diffusion potential while others suggest the voltage to be an adsorption potential (1). Teorell (2,3) considered the presence of charge on the membrane skeleton responsible for the development of potential across it. Based of fixed charge concept a number of theoretical equations for membrane potential, developed across a charged membrane separating two electrolytic solutions, have been derived and tested using, generally, model membranes.

In this chapter, the evaluation of effective fixed charge density of polystyrene based nickel and cobalt phosphate membranes from potential measurements and using the most recently developed methods of Kobatake et al. (4-15), and Tasaka et al. (16) including the generally used and widely accepted method of Teorell-Meyer and Sievers, (TMS) are described. This is in order to substantiate our earlier findings, on the basis of Eisenman-Sherry model of membrane selectivity. That polystyrene based membranes possess small density of fixed charge groups on the membrane matrix as well as to test the validity of the recently developed theories for membrane potential.

Experimental

The membrane was prepared by the method suggested by Beg and co-workers (17-19). Nickel phosphate and cobalt phosphate precipitates was prepared by mixing a 0.2 M nickel (II) chloride and 0.2 M cobalt (II) chloride with 0.2 M tisodium phosphate solution. The precipitate was well washed with deionized water to remove free electrolyte and dried at room temperature. The precipitate was ground into fine powder and was sieved through 200 mesh (granule size 0.07 mm). Pure amorphous polystyrene (cross linked with 1% divinyl benzene and obtained from Fluka product number 81535) were also ground and sieved. Different proportions of polystyrene and nickel and cobalt phosphate precipitates were mixed thoroughly using grinder. The mixture was then kept into the cast die having diameter 2.45 cm and placed in an oven maintained at 200°C for about half an hour to equilibrate. The die containing the mixture was they transferred swiftly to a pressure device (Spectra Lab. Model SL. 89 UK) and various pressures such as 4, 5, 6, 7 or 8 T were applied during the formation of the membranes. As a result nickel and cobalt phosphate membranes of approximate thicknesses 0.095. 0.090. 0.085. 0.080 and 0.075 cm were obtained, respectively. Our effort has been to get the membrane of adequate chemical and mechanical stability. Thus, the membranes prepared by mixing 25% of polystyrene was found to be mechanically stable and was quite suitable for our studies. Those containing larger amount (>25%) of polystyrene did not give reproducible results, while those containing lesser amount (<25%) were unstable. The total amount of the mixture, thus, utilized for the preparation of the membrane contain 0.125 gm of polystyrene and 0.375 gm of nickel and cobalt phosphate.



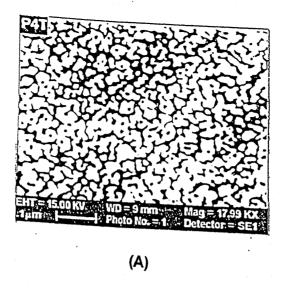
were used for measuring membrane potentials. The reference electrodes used were reversible Ag-AgCl standing in chloride solutions. The total potential difference between Ag-AgCl electrodes placed on either side of the membrane is the algebraic sum of the electrode potential i.e., concentration potential and the membrane potential Em (20, 21). A tenfold difference in concentration of chloride solutions (i.e., $C_2/C_1 = 10$) was maintained and measurements were made by a pye-precision potentiometer (No. 7568). The solutions were replaced by fresh solutions and when there was no change in potential with the addition of fresh solutions, with constant vigorous stirring by a pairs of magnetic stirrers, it was taken as the true total potential difference across the Ag-AgCl electrodes. In all the four membrane it could be reproduced within a few tenths of a mV. The whole cell was immersed in a water thermostat maintained at 25 \pm 0.1°C. The various salt solutions (chlorides of Li^{\dagger} , Na^{+} and K^{+}) were prepared from BDH, AR grade chemicals and deionized water.

Results and Discussion

of number investigators while developing precipitates/ membranes have frequently utilized scanning electron microscope (SEM) micrographs for their characterization (22,23). The composite pore structure, micro/macro porosity, homogeneity, thickness, cracks and surface texture/morphology have been specially studied by scanning electron microscopy (24, 25). The information obtained from microscopic photographs/images have provided guidance in the preparation of well ordered precipitates and/or crack-free membranes. Consequently, the SEM surface images of the polystyrene based nickel phosphate and cobalt phosphate membranes were taken at pressure P4T and P6T respectively. These are presented in Fig. 1.1 SEM images appear to be composed of dense and loose aggregation of small particles and formed pores probably with non-linear channel but not fully interconnected. Particles are irregularly condensed and adopt a heterogeneous structure composed of masses of various size. The surface openings also seem to decrease with increasing applied pressure.

The values of membrane potential E_m measured across cobalt phosphate and nickel phosphate membranes are given in Tables 1.1 and 1.2 and are also plotted in Figs. 1.2 and 1.3 against log (C₁ + C₂)/2.

Polystyrene based inorganic precipitate membranes have the ability to generate potentials when they are used to separate electrolyte solutions of different concentrations (26-35). This property is attributed to the presence of a net charge on the membrane probably due to adsorption of anions or cations. The quantity of charge required to generate potentials, particularly when dilute solutions are used, is small. This, of course, is dependent on the porosity of the membrane. If the membrane pores are too wide, any amount of charge on the membrane



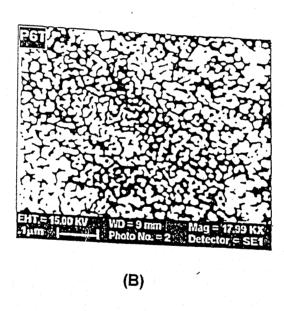


Fig.1.1

SEM images of polystyrene based (A) nickel phosphate and (B) cobalt phosphate membranes.

Table 1.1

The values of the observed membrane potential E_m (mv) across polystyrene based cobalt phosphate membrane at $25\pm0.1^{\circ}C$.

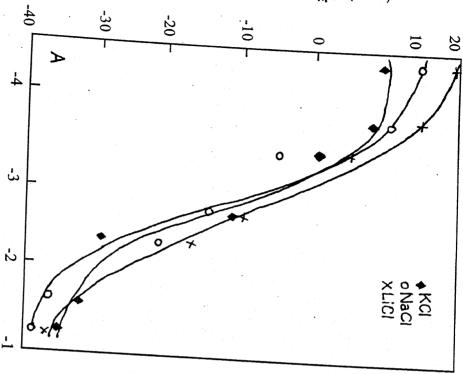
Electrolyte	KCl	NaCl	LiCl
Concentration/mol l ⁻¹			
C_2/C_1			
$1 \times 10^{-1} / 1 \times 10^{-2}$	-34.2	-38.6	-34.9
$5 \times 10^{-2} / 5 \times 10^{-3}$	-31.3	-36.7	32.5
$1 \times 10^{-2} / 1 \times 10^{-3}$	-28.4	-21.6	-16.3
$5 \times 10^{-3} / 5 \times 10^{-4}$	-10.2	-14.4	-10.3
$1 \times 10^{-3} / 1 \times 10^{-4}$	1.6	-5.1	5.1
$5 \times 10^{-4} / 5 \times 10^{-5}$	9.1	9.9	15.4
$1 \times 10^{-4} / 1 \times 10^{-5}$	9.9	14.9	19.9

Table 1.2

The values of the observed membrane potential e_m (mv) across polystyrene based nickel phosphate membrane at $25\pm0.1^{\circ}C$.

Electro	lyte	KCl	NaCl	LiCl
Concen	tration/mol I ⁻¹)			
C_2/C_1				
	1 x 10 ⁻¹ /1 x 10 ⁻²	-42.3	-39.9	-40.4
	$5 \times 10^{-2} / 5 \times 10^{-3}$	-40.2	-40.2	-37.9
	$1 \times 10^{-2} / 1 \times 10^{-3}$	-31.9	-24.4	-21.4
	$5 \times 10^{-3} / 5 \times 10^{-4}$	-14.9	-12.9	-6.8
	1 x 10 ⁻³ / 1 x 10 ⁻⁴	1.4	9.1	4.4
	$5 \times 10^{-4} / 5 \times 10^{-5}$	10.2	10.2	7.9
	1 x 10 ⁻⁴ / 1 x 10 ⁻⁵	12.4	12.4	15.2





 $\log \left(C_1 + C_2\right)/2$

Fig. 1.2

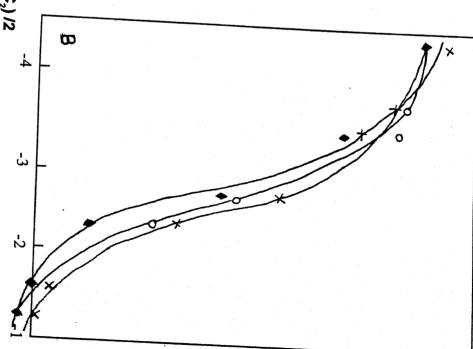


Fig. 1.3

polystyrene based (A) cobalt phosphate and (B) nickel phosphate membranes.

Plots membrane potential E_m (mV) against log $(C_2 + C_2)/2$ using 1:1 electrolytes across

does little to generate good potentials. But if the membrane pores are narrow, a little charge on it can give ideal potentials according to the Nernst-equation.

$$E_{\text{max}} = \frac{RT}{F} \ln a_1/a_2 \tag{1.1}$$

Where at and at are the activities of the two solutions on either side of the membrane, Emax is the membrane potential and R,T and F have their usual significance.

An interesting point with the value of Em for cobalt and nickel phosphate polystyrene based membranes is the fact that these are positive when the membrane is separating dilute solutions of the electrolytes (i.e., dilute side C1 taken as Positive). This means that the membrane is cation selective, and when the membrane is used to separate concentrated solutions, the values of Em are Negative, i.e., and the membrane becomes anion selective. Such reversal in selectivity character is not peculiar to these systems (27).

Two important factors, which control electrolyte permeability through a membrane, are charge on the membrane and its porosity. Parchment paper, except for the presence of some stray and end carboxylic group, contains very few fixed groups. Deposition of inorganic precipitate gives rise to a net negative charge on membrane surface in the dilute solutions of a 1:1 electrolyte leading to the type of ionic distribution associated with the electrical double layer (20). The stepwise change in membrane potential or the selectivity character of the membrane-electrolyte system may readily be explained in terms of the

structural changes produced in the electrical double layer at the interfaces.

The fixed groups present in well-characterized ion-exchange membranes can be easily estimated by titration. This procedure was used by Sollner et al. (37) to estimate the end groups and stray carboxylic groups present in the collodion material. Lakshminarayanaiah (38) in his studies with thin membranes of parlodion, used two methods-the isotopic and the potentio-metric to evaluate the apparent fixed charge on the membrane material. In the present studies the titration method proved inconvenient and very inaccurate, while the isotopic method was discarded in view of the strong ionic adsorption phenomena exhibited by these systems. Consequently the potentiometric method was used. This method is based on the fixed charge theory of membrane potential proposed simultaneously by Teorell (2,3), and Meyer and Sievers (39). The fixed charge concept of Teorell (2,3) and Meyer and Sievers (39) (the TMS theory) for charged membranes is a pertinent starting point for the investigation of the actual mechanisms of the ionic or molecular processes, which occur in the membrane phase. According to this theory membrane potential is considered to be composed of two Donnan potential at the two solution membrane interfaces and a diffusion potential arising from unequal concentration of the two membrane phases. These authors derived following equation for membrane potential in millivolts (at 25°C) applicable to a highly idealized system, viz:

$$E_{m} = 59.2 \left[log \frac{C_{2}}{C_{1}} \frac{\left(\sqrt{4C_{1}^{2} + \overline{X}^{2}} + \overline{X} \right)}{\left(\sqrt{4C_{2}^{2} + \overline{X}^{2}} + \overline{X} \right)} + \overline{U} log \frac{\sqrt{4C_{2}^{2} + \overline{X}^{2}} + \overline{X}\overline{U}}{\sqrt{4C_{1}^{2} + \overline{X}^{2}} + \overline{X}\overline{U}} \right]$$
(1.2)

where $\overline{U} = (\overline{u} - \overline{v}) / (\overline{u} + \overline{v}), \overline{u}$ and \overline{v} are the mobilities of cation and anion respectively in the membrane phase; \overline{X} is charge on the membrane expressed in equivalents/liter of imbibed solution. Equation (1.2) has been frequently used for the evaluation of the fixed charge density \overline{X} of a membrane (20). In order to evaluate this parameter for the simple case of 1:1 electrolyte and membrane carrying a net negative charge of unity $(\overline{X}=1)$, theoretical concentration potentials E_m existing across the membrane are calculated as function C2, are given in Table 1.3. The ratio C_2/C_1 being kept at constant value for different mobility ratios, $\overline{u}/\overline{v}$. The observed membrane potential values are then plotted in the same graph as a function of 1/C2 (Fig. 1.4, 1.5). However, hypothetical Potential profiles existing across polystyrene based membranes are also shown in Fig. 1.6. The experimental curve is shifted horizontally until it coincides with one of the theoretical curves. The extent of this shift gives $\log \overline{X}$ and the coinciding theoretical curve, the value of u/v, Figs. (1.7 and 1.8). In the case of cobalt and nickel phosphate membranes the observed membrane potential curves on shifting horizontally did not overlap with any of the theoretical curves particularly in the dilute ranges. As a result eq. (1.2) was used in another way, in the way Teorell did, to evaluate \overline{X} . A family of theoretical curves (Figs. 1.7 and 1.8) were constructed assigning \overline{X} =1 and successively decreasing values to \overline{X} (\overline{X} <1) keeping $\overline{u}/\overline{v} = 0.2$ (Table 1.5). The curves thus obtained have same shape and limit but are transposed along the log C_2 axis. The value of \overline{X} is then give by the curve with which the experimental curve coincided. The values thus derived are given in (Table 1.4). In addition to the value of \overline{X} , the plotting in this form correctly predicts diffusion potential at the limit \overline{X} = 0. The diffusion potential values derived in this way were found to

Table 1.3

Theoretical values of membrane potential Em (mV) calculated from Teorell-Meyer-Sievers method for different mobility ratio $\overline{u}/\overline{v}$ and $(\overline{X}=1)$ at different concentrations

N. H L 112.								
Mobility ratio u/v	0.7	0.4	9.0	8.0	1.0	1.2	4.	1.6
Concentration/mol I-1								
C2/C1					. *	•		
$1 \times 10^{1} / 1$	-35.0	-22.5	-3.0	8.3	15.3	16.1	20.2	23.5
$5/5 \times 10^{-1}$	-22.5	10.0	25.0	30.8	40.7	20.1	30.2	30.0
$1/1 \times 10^{-1}$	15.0	30.0	45.2	46.0	45.0	34.0	37.5	45.2
$5 \times 10^{-1} / 5 \times 10^{-2}$	35.0	40.0	47.5	47.2	50.2	50.0	53.0	55.0
$1 \times 10^{-1} / 1 \times 10^{-2}$	20.0	50.0	50.0	55.5	55.0	55.0	57.0	58.8
$5 \times 10^{-1} / 1 \times 10^{-2}$	58.0	57.0	55.0	58.0	59.0	59.2	59.4	0.09
$1 \times 10^{-1} / 1 \times 10^{-2}$	59.0	59.0	59.0	59.0	59.9	59.9	0.09	0.09
$5 \times 10^{-1}/1 \times 10^{-2}$	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09
$1 \times 10^{-1}/1 \times 10^{-2}$	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09

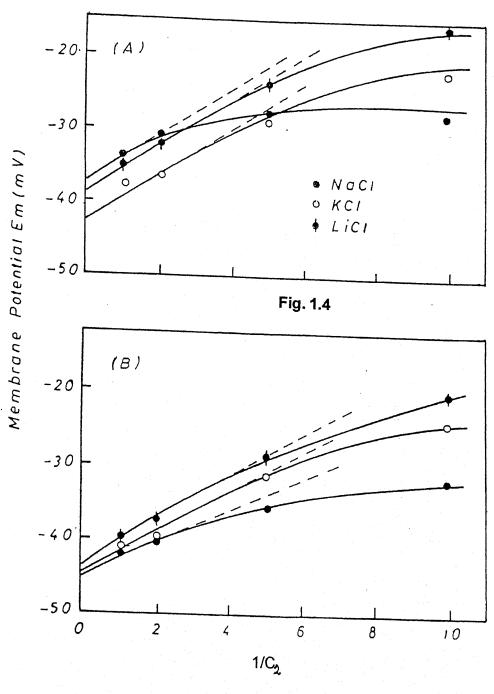


Fig. 1.5

Plots of membrane E_m (mV) against $1/C_2$ for polystyrene based (A) cobalt phosphate and (B) nickel phosphate membranes.

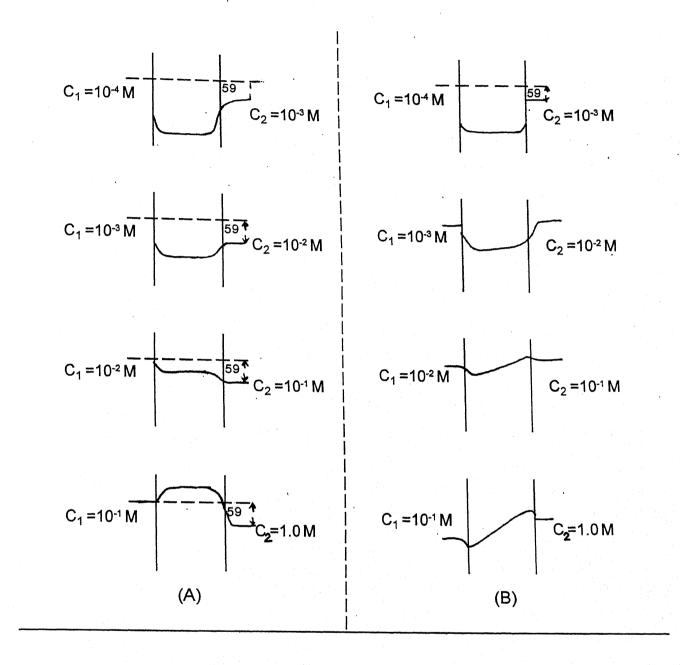


Fig.1.6

(A, B) Hypothetical potential profiles existing across polystyrene based membranes.

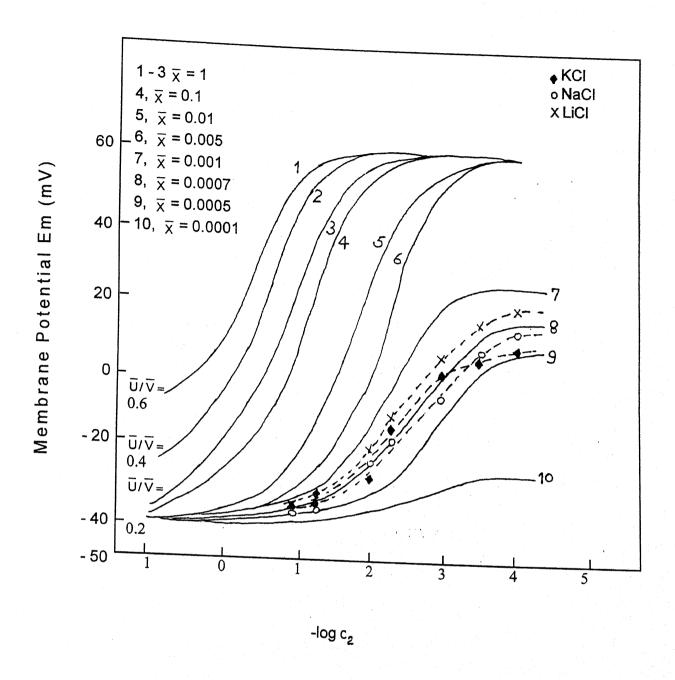


Fig. 1.7

Smooth curves are the theoretical concentration potentials for \overline{X} = 1 and different mobility ratios \overline{U} / \overline{V} , (1 - 3), and \overline{X} < 1 (4-10) for \overline{U} / \overline{V} = 0.2 broken lines are experimental values of E_m (mV) for various 1:1 electrolytes across polystyrene based cobalt phosphate membrane.

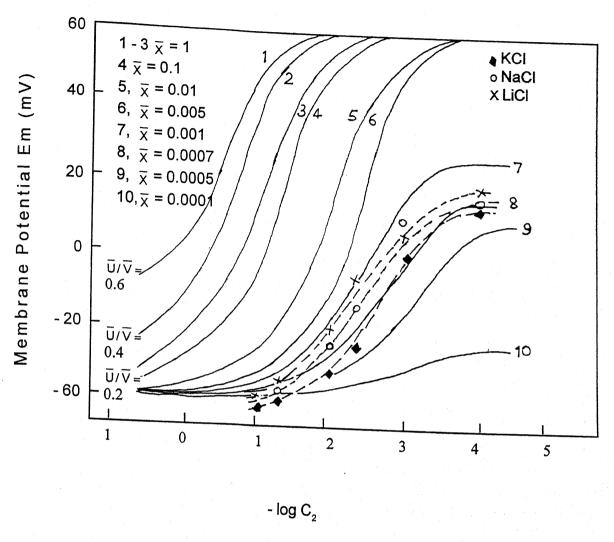


Fig. 1.8

Smooth curves are the theoretical concentration potentials for \overline{X} = 1 and different mobility ratios \overline{U} / \overline{V} , (1 - 3), and \overline{X} < 1 (4-10) for \overline{U} / \overline{V} = 0.2 broken lines are experimental values of E_m (mV) for various 1:1 electrolytes across polystyrene based nickel phosphate membrane

have approximately the same magnitude and sign as the potential across the membranes when these are used to separate highly concentrated solutions of an electrolyte (Table 1.4). In view of this limiting diffusion potential value, the variation in membrane potential across cobalt and nickel phosphate membranes with the change in external electrolyte concentrations may be ascribed to be due to the structural changes produced in the electrical double layer at the membrane-solution interfaces. Thus cobalt, nickel phosphate membrane electrolyte systems may be more conveniently described as consisting of two mini cells - one with constant e.m.f. corresponding to the limiting diffusion potential and the other with variable e.m.f. representing the interfacial potential difference (0 to 60 mV approximately). Since the total membrane potential changes sign as the concentration of the electrolytes across the membranes are changed, it may be concluded that these mini cells are combined together in series but operating in opposite direction and that the membrane-solution interface seems to be the rate determining step as suggested by Tien and Ting (40) for bilayer membranes.

Kobatake et al. (7) on the basis of the thermodynamics of irreversible processes derived the following equation for the electrical potential E_m which arises when a negatively charged membrane separates two solutions of a 1:1 electrolyte of concentrations C₁ and C₂ (C1 < C2):

$$E_{\rm m} = -\frac{RT}{F} \left[\frac{1}{\beta} \ln \frac{C_2}{C_1} - (1 + \frac{1}{\beta} - 2\alpha) \ln \left(\frac{C_2 + \alpha\beta \overline{X}}{C_1 + \alpha\beta \overline{X}} \right) \right]$$
(1.3)

Where $\alpha = U/(u + v)$

$$\beta = 1 + KF\overline{X}/u$$

Table 1.4

Values of membrane charge density \overline{X} (eq/l), mobility ratio ($\overline{U}/\overline{V}$) and diffusion potential (mV) for various membrane electrolyte system using Teorell-Meyer-Sievers Theory at 25 ± 0.1 °C

Electrolyte	Parameters	KCl	NI CI	
Membranes		IXCI	NaCl	LiCl
Cobalt	$(\overline{X}) \times 10^3$	1.5	1.8	2.8
phosphate				
	(u/v)	0.2	0.2	0.2
Nickel	(Diff. Pot.)	-34.2	-38.5	-34.5
phosphate	$(\overline{X}) \times 10^3$	1.7	1.3	2.4
-	(u/v)	0.2	0.0	
	(Diff. Pot.)	-42.3	0.2 -42.2	0.2 -40.4

Table 1.5

Theoretical values of membrane potential E_{m} (mV) calculated from Teorell-Meyer-Sievers method for different value

of \overline{X} and $\overline{u}/\overline{v} = 0.2$.

Charge density (\overline{X})	0.1	0.01	0.005	0.001	1.0007	1.0005	1.0001
Concentration/mol I ⁻¹							
C_2/C_1							
$1 \times 10^{1} / 1$	-39.1	-39.8	-39.1	-39.1	-39.1	-39.8	-39.1
$5/5 \times 10^{-1}$	-39.1	-39.7	-39.1	-39.1	-39.1	-39.8	-39.1
$1/5 \times 10^{-1}$	-21.9	-37.3	-38.2	-38.2	-39.0	-39.0	-39.0
$5 \times 10^{-1} / 5 \times 10^{-2}$	-8.1	-36.4	-36.8	-36.2	-37.8	-39.0	-39.1
$1 \times 10^{-1} / 1 \times 10^{-2}$	31.1	-30.7	-33.7	-35.2	-34.8	-37.5	-38.0
$5 \times 10^{-2} / 1 \times 10^{-3}$	50.3	-2.2	-10.5	-30.7	-24.3	-28.5	-37.4
$1 \times 10^{-2} / 1 \times 10^{-3}$	59.2	21.5	21.8	10.5	-10.0	-22.0	-30.0
$5 \times 10^{-3}/1 \times 10^{-4}$	59.5	41.3	54.7	21.5	9.1	-20.0	26.9
1 x 10 ⁻³ /1 x 10 ⁻⁴	59.5	59.5	58.0	24.5	15.2	-19.5	-25.5

F and K represent, respectively, the Faraday constant and a constant dependent upon the viscosity of the solution and structural details of the polymer network of which the membrane is composed. To evaluate the membrane parameters, α , β and \overline{X} , two limiting forms of the above equation were derived. When the external salt concentration C is sufficiently small.

$$\left| E_m^{\sigma} \right| = \frac{1}{\beta} \ln \gamma - \left(\frac{\gamma - 1}{\alpha \beta \gamma} \right) \left(1 + \frac{1}{\beta} - 2\alpha \right) \left(\frac{C_2}{\overline{X}} \right) + \dots$$
(1.4)

Where $\left|E_{m}^{\sigma}\right| = \text{F E}_{m}/\text{RT}$ and $\gamma = \text{C}_{2}/\text{C}_{1}$

When the salt concentration C is high.

$$\frac{1}{t_{-}} = \frac{1}{1-\alpha} + \frac{(1+\beta-2\alpha\beta)(\gamma-1)\alpha}{2(1-\alpha)^{2} \ln \gamma} (\frac{\overline{X}}{C_{2}}) + \dots$$
 (1.5)

Where t_ is the apparent transference number of coions (anions) in a negatively charged membrane defined by

$$\left| E_m^{\sigma} \right| = (1 - 2t_{-}) \ln \gamma \tag{1.6}$$

The value of t_{-} calculated from observed membrane potentials using eq. (1.6) for cobalt and nickel phosphate membranes, are given in Tables 1.6 and 1.7. Equation (1.4) was used to give the value of β (see Table 1.8) and

Table 1.6

Transference number t_ of coins from observed membrane potential at various electrolyte concentration across polystyrene based cobalt phosphate membrane

Electrolyte	TZCI		
Concentration/mol I ⁻¹	KCl	NaCl	LiCl
C_2/C_1			
1 x 10 ⁻¹ /1 x 10 ⁻²	0.68	0.70	
$5 \times 10^{-2} / 5 \times 10^{-3}$	0.65	0.72	0.71
$1 \times 10^{-2} / 1 \times 10^{-3}$	1	0.70	0.67
	0.64	0.58	0.53
$5 \times 10^{-3} / 5 \times 10^{-4}$	0.50	0.52	0.40
$1 \times 10^{-3} / 1 \times 10^{-4}$	0.39	0.44	
$5 \times 10^{-4} / 5 \times 10^{-5}$	0.32		0.35
$1 \times 10^{-4} / 1 \times 10^{-5}$		0.31	0.27
T X 10 / 1 X 10-5	0.31	0.27	0.23

Table 1.7

Transference number t_ of coins from observed membrane potential at various electrolyte concentration across polystyrene based nickel phosphate membrane

Electrolyte	KCl	NaCl	Tich
Concentration/mol l ⁻¹		NaCi	LiCl
C_2/C_1			
$1 \times 10^{-1} / 1 \times 10^{-2}$	0.75	0.75	0.74
$5 \times 10^{-2} / 5 \times 10^{-3}$	0.73	0.74	0.72
$1 \times 10^{-2} / 1 \times 10^{-3}$	0.66	0.60	0.72
$5 \times 10^{-3} / 5 \times 10^{-4}$	0.52	0.50	0.45
$1 \times 10^{-3} / 1 \times 10^{-4}$	0.36	0.32	0.36
$5 \times 10^{-4} / 5 \times 10^{-5}$	0.31	0.31	0.33
1 x 10 ⁻⁴ / 1 x 10 ⁻⁵	0.29	0.24	0.33

Table 1.8

Values of the membrane parameters α and β for various membrane electrolyte system at $~\gamma$ =10

Electrolyte	KC	Cl	Na	Cl	Lie	Cl
Membranes	α	β	α	β	α	β
Cobalt	0.18	1.2	0.17	1.2	0.16	1.2
Phosphate	•		•			
Nickel	0.11	1.5	0.13	1.5	0.14	1.5
Phosphate						

Table 1.9

Values of the effective fixed charge density \overline{X} (eq/l) using Kobatake's method for various membrane electolyte system at 25± 0.1° C

Electrolyte	KCl	NaCl	LiCl
Membranes			
Cobalt	5.3	2.5	3.7
phosphate			
$(\overline{X}) \times 10^3$, eq/1			
Nickel phosphate	1.9	4.7	4.2
$(\overline{X}) \times 10^3$, eq/1			

a relation between α and \overline{X} by evaluating the intercept and the initial slope of the plot of $\left|E_m^\sigma\right|$ against C2 (Figs. 1.9 and 1.10), while eq. (1.5) was used to evaluate α (See Table 1.8) from the intercept of a plot of $1/t_-$ against $1/C_2$ (Figs. 1.11 and 1.12). The values of \overline{X} were determined by inserting this value of α in the relation between α and \overline{X} obtained earlier. The values of \overline{X} derived in this way for the membranes and 1:1 electrolytes are given in Table 1.9.

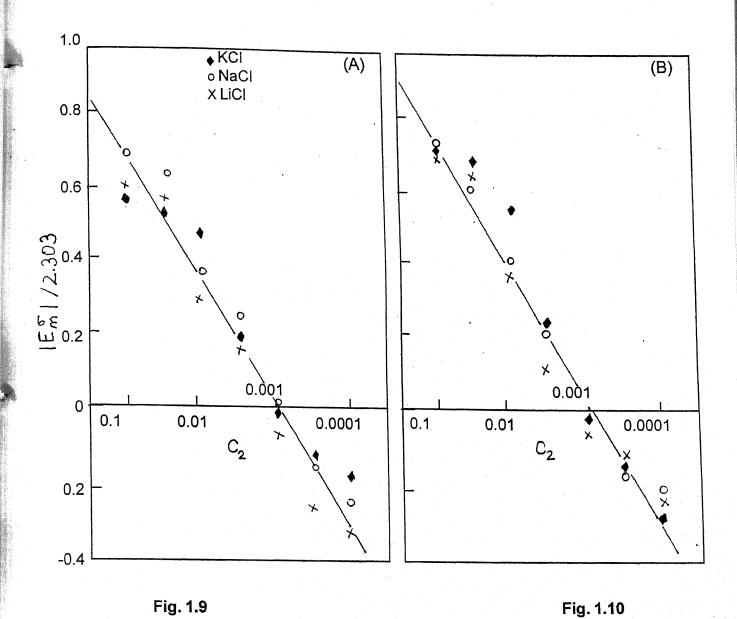
Once the values of the parameters α,β and \overline{X} for a given membrane-electrolyte system have been determined one can get the theoretical E_m vs. C_2 curve using eq. (1.3) for any given $\gamma = (C_2/C_1)$ and compare it with the corresponding experimental data. For this comparison eq. (1.3) can be rewritten in the following form as suggested by Kobatake and Coworkers (7).

$$\frac{(\gamma - e^q)}{(e^q - 1)} = Z \tag{1.7}$$

With q and Z defined by

$$q = \frac{\left|E_m^{\sigma}\right| + (1 - 2\alpha) \ln \gamma}{1/\beta + (1 - 2\alpha)}$$

and $Z = C_2/\alpha\beta \overline{X}$. Thus if eq. (1.7) is valid the value of $(\gamma - e^q)/(e^q - 1)$ calculated from the measured E_m with predetermined α, β and \overline{X} and the given value of γ must fall on a straight line which has a unit slop and passes the co-ordinate origin when plotted against Z. This behavior



Plots of $|E|_{\mathfrak{m}}^{\sigma}|$ 1/2.303 against C_2 for polystyrene based (A) cobalt phosphate and (B) nickel phosphate membranes in contact with various 1:1 electrolyte solutions.

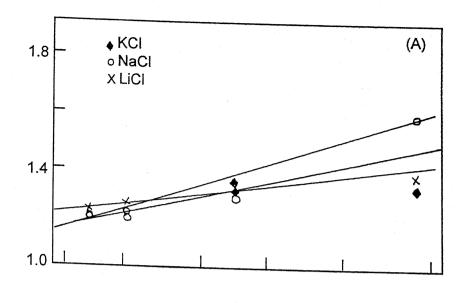


Fig. 1.11

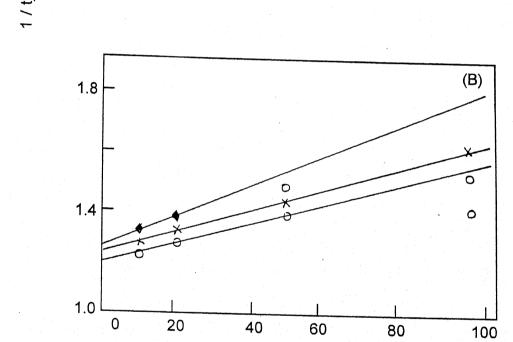


Fig. 1.12

1/ C₂

Plots of 1/t_ against 1/C $_2$ for polystyrene based (A) cobalt phosphate and (B) nickel phosphate membranes using 1:1 electrolyte solutions at constant γ (γ =10).

should be observed irrespective of the value of γ and the kind of membrane-electrolyte system used.

Recently Kobatake and Kamo (12) derived another equation eq. (1.8) for the membrane potential starting with the basic flow equation provided by the thermodynamics of irreversible processes and using a different set of assumptions: namely, (a) the contribution of mass movement is negligible (12), and (b) small ions do not behave ideally in a charged membrane (12). Their result is:

$$E_{m} = -\frac{RT}{F} \left[\ln \frac{C_{2}}{C_{1}} + (2\alpha - 1) \ln \frac{\sqrt{4C_{2}^{2} + \phi^{2}X^{2}} + (2\alpha - 1)\phi X}{\sqrt{4C_{1}^{2} + \phi^{2}X^{2}} + (2\alpha - 1)\phi X} - \ln \frac{\sqrt{4C_{2}^{2} + \phi^{2}X^{2}} + \phi X}{\sqrt{4C_{1}^{2} + \phi^{2}X^{2}} + \phi X} \right]$$
(1.8)

Where ϕ is a characteristic factor of the membrane -electrolyte pair, and represents the fraction of counter ions not tightly bound to the membrane skeleton. The product ϕX is termed the thermodynamically effective fixed charge density of a membrane, the other terms have their usual significance. Equation 1.8 reduces to the TMS membrane potential for $\phi = 1$. Since it is somewhat troublesome to evaluate ϕX at an arbitrary external electrolyte concentration from the observed membrane potential using eq. (1.8), Kobatake and Kamo (12) have proposed a simple method using the following approximate equation for the diffusive contribution to the e.m.f of a cell with transport.:

$$E_{\rm m} = -\frac{RT}{F} (1 - 2t_{-app}) \ln (C_2/C_1)$$
 (1.9)

Where t_{app} is the apparent transference number of coions in the membrane phase. Comparison of eqs. (1.8) and (1.9) gives

$$t_{-app} = \frac{1-2a}{2} \frac{\ln(\frac{\sqrt{4\xi_{2}^{2}+1}+2\alpha-1}{\sqrt{4\xi_{1}^{2}+1}+2\alpha-1} + \frac{\ln(\frac{\sqrt{4\xi_{2}^{2}+1}+1}{\sqrt{4\xi_{1}^{2}+1}+1})}{\ln\gamma} + \frac{\ln(\frac{\sqrt{4\xi_{2}^{2}+1}+1}{\sqrt{4\xi_{1}^{2}+1}+1})}{2\ln\gamma}$$
(1.10)

Where $\xi = C/\phi X$

On the other hand (11,12), the mass fixed transference number of coions in a negatively charged membrane immersed in an electrolyte solution of concentration C was defined by

$$t_{-} = v\overline{C}_{-} / (u \overline{C}_{+} + v\overline{C}_{-})$$
(1.11)

Where \overline{C}_+ and \overline{C}_- are the concentrations of cation and anion, respectively, in the membrane phase. This equation was transformed to

$$t_{-} = 1 - \alpha \frac{\sqrt{4\xi^2 + 1} + 1}{\sqrt{4\xi^2 + 1} + (2\alpha - 1)}$$
 (1.12)

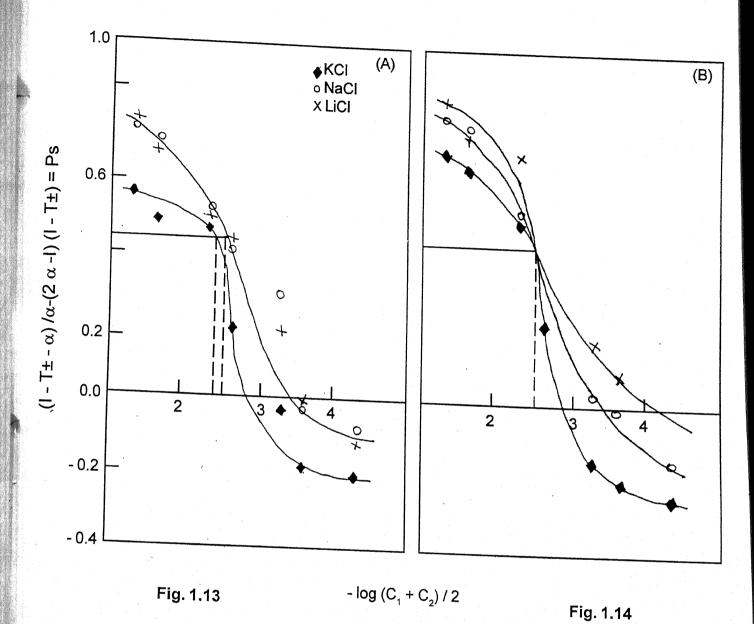
using certain equations for the activity coefficients, mobilities of small ions in the membrane phase, and the equilibrium condition for electrical neutrality (11,12). The difference between the apparent transference number t_{-app} calculated from eq. (1.10) and t_ from eq. (1.12) for various reduced concentrations ξ (ξ = C/ ϕ X) was found to be always less than 2% over a wide range of external electrolyte concentrations. Therefore, t_{-app} and t_ were considered practically the same. As a result, the apparent transference number evaluated from the membrane potential data was used for the determination of the thermodynamically effective

fixed charge density ϕX of the membrane at a given average salt concentration C (C = (C₁ + C₂)/2) using eq. (1.12) At the same time rearrangement of eq. (1.12) provides a definition of perm selectivity P_s , given by the expression

$$\frac{1}{(4\xi^2+1)^{1/2}} = \frac{1-t_--\alpha}{\alpha-(2\alpha-1)(1-t_-)} = P_s$$
 (1.13)

This equation can be used to find the perm-selectivity from membrane potential measurements using eq. (1.9). If the transport number of coions $(t_{-} \text{ or } t_{-app})$ is zero, the membrane is perfectly selective and Ps =1, while if the transport number of coions has the value in free solution P_s =0. The values of Ps obtained in Tables (1.10 and 1.11) using the right hand side of eq. (1.13) were plotted against log C. The concentration at which Ps (where $\xi = C/\phi X = 1$ becomes $(1/5)^{1/2}$ gives the value thermodynamically effect fixed charge density \$\phi X\$ as required by the left side of eq. (1.13). Figures 1.13 and 1.14 represent plots of Ps versus log (C₁+C₂)/2 for the polystyrene based cobalt and nickel phosphate membranes in contact with various 1:1 electrolytes. The value of ϕX thus derived for the membranes and 1:1 electrolyte combinations are given in Table 1.12.

More recently. Tasaka et al. (16) derived an equation for the membrane potential existing across a charged membrane. The total membrane potential E_m was considered as the sum of a diffusion potential E_d inside the membrane and the electrostatic potential differences E_e between the membrane surfaces and the electrolyte solutions on both sides of the membrane. The diffusion potential E_d was obtained by integrating the basic flow equation for diffusion (41), while



Plots of Ps against - $\log (C_1 + C_2)/2$ for polystyrene based (A) cobalt phosphate and (B) nickel phosphate membranes

Table 1.10

Value of perm selectivity P_s of the membrane using various 1:1 electrolytes at different concentration for polystyrene based cobalt phosphate membrane

Electrolyte	KCl	NaCl	LiCl
Concentration/mol l ⁻¹			
C_2/C_1			
1 x 10 ⁻¹ /1 x 10 ⁻²	0.46	0.65	0.67
$5 \times 10^{-2} / 5 \times 10^{-3}$	0.40	0.61	0.60
$1 \times 10^{-2} / 1 \times 10^{-3}$	0.38	0.43	0.39
$5 \times 10^{-3} / 5 \times 10^{-4}$	0.10	0.32	0.33
$1 \times 10^{-3} / 1 \times 10^{-4}$	0.10	0.20	0.09
$5 \times 10^{-4} / 5 \times 10^{-5}$	0.06	-0.02	0.00
$1 \times 10^{-4} / 1 \times 10^{-5}$	0.08	-0.05	-0.20

Table 1.11

Value of perm selectivity P_s of the membrane using various 1:1 electrolytes at different concentration for poly styrene based nickel phosphate membrane

Electrolyte	KCl	NaCl	LiCl
Concentration/mol l ⁻¹			
C_2/C_1			
1 x 10 ⁻¹ / 1 x 10 ⁻²	0.60	0.69	0.74
$5 \times 10^{-2} / 5 \times 10^{-3}$	0.56	0.68	0.67
$1 \times 10^{-2} / 1 \times 10^{-3}$	0.42	0.44	0.59
$5 \times 10^{-3} / 5 \times 10^{-4}$	0.14	0.29	0.25
$1 \times 10^{-3} / 1 \times 10^{-4}$	-0.02	0.04	0.09
$5 \times 10^{-4} / 5 \times 10^{-5}$	-0.08	0.02	0.02
$1 \times 10^{-4} / 1 \times 10^{-5}$	0.012	-0.12	0.00

the electrostatic potential difference was calculated from the Donnan's theory, Stated mathematically.

$$E_{\rm m} = E_{\rm d} + E_{\rm e} \tag{1.14a}$$

Where

$$-E_d = -\int_1^2 \frac{Jo}{F\,\overline{C}\,o}\,\frac{\phi\,X}{(\overline{C}_- + \phi X)u + \overline{C}_- v}\,dx + \frac{RT}{F}\,\int_1^2 \frac{(\overline{C}_- + \phi X)u}{(\overline{C}_- + \phi X)u + \overline{C}_- v}\,d\ln\,\overline{a}_+ - \frac{1}{2}\frac{(\overline{C}_- + \phi X)u}{(\overline{C}_- + \phi X)u + \overline{C}_- v}\,dx$$

$$\frac{RT}{F} \int_{1}^{2} \frac{\overline{C}_{v}}{(\overline{C} + \varphi X)u + \overline{C}_{v}} d \ln \overline{a}_{-}$$
 (1.14 b)

and

$$-\mathbf{E}_{e} = -\frac{RT}{F} \ln(\frac{\overline{a_{1}}}{a_{1}} \frac{a_{2}}{\overline{a_{2}}})$$
 (1.14c)

where at and at are the activities of the electrolytes on the two sides of the membrane, the overbar refers to the phenomena in the membrane phase. Jo is the flow of electrolyte in the absence of an external electrolyte field, the other symbol have their usual significance. On integrating eq. (1.14) in the limit of high electrolyte concentrations across the membrane, one obtains the following equation for the membrane potential.

$$-\mathbf{E}_{\mathbf{m}} = \frac{RT}{F} \left(\frac{\phi X}{2}\right) \left(\frac{\gamma - 1}{\gamma}\right) \frac{1}{C_2} + \frac{RT}{F} \left(\frac{u - v}{u + v}\right) \left[\frac{1 - \frac{\phi XJo}{RT\overline{C}o(u - v)K}}{1 - \frac{\phi XJo}{2RT\overline{C}ovK}}\right] \ln \gamma$$

$$+\frac{RT\phi X}{2Fuv}\left(\frac{Jo}{RT\overline{C}oK}\right)^{2} \qquad \frac{\left[1-\frac{\phi XJo \quad (u+v)}{4RT\overline{C}ouvK}\right]}{\left(1-\frac{\phi XJo}{2RT\overline{C}ovK}\right)^{2}}\left(\gamma-1\right)C_{2} \qquad (1.15)$$

At high electrolyte concentrations, eq. (1.15) can be approximated by

$$-E_{\rm m} = \frac{RT}{F} \frac{(\gamma - 1)}{\gamma} (\frac{\phi X}{2}) 1/C_2 + \dots$$
 (1.16)

Equation (1.16) predicts a linear relationship between E_m and $1/C_2$ from which ϕX can be calculated. Plots of E_m versus $1/C_2$ for the membranes are represented in Figs. 1.15 and 1.16 sets of straight lines in agreement with eq. (1.16) are obtained. The values of ϕX derived from the slops of the lines are given in Table 1.13.

It is noted from Tables 1.5,1.9, 1.12 and 1.13 that the charge densities of the membrane electrolyte system are low. This is in accordance with our earlier findings of diffusion rate studies. Further, the values derived from different methods are almost the same. A little difference may be attributed to the different procedures adopted. It is concluded, therefore, that the methods developed recently by kobatake et al. and Tasaka et al. for the evaluation of effective fixed charge density are valid for the systems under investigation.

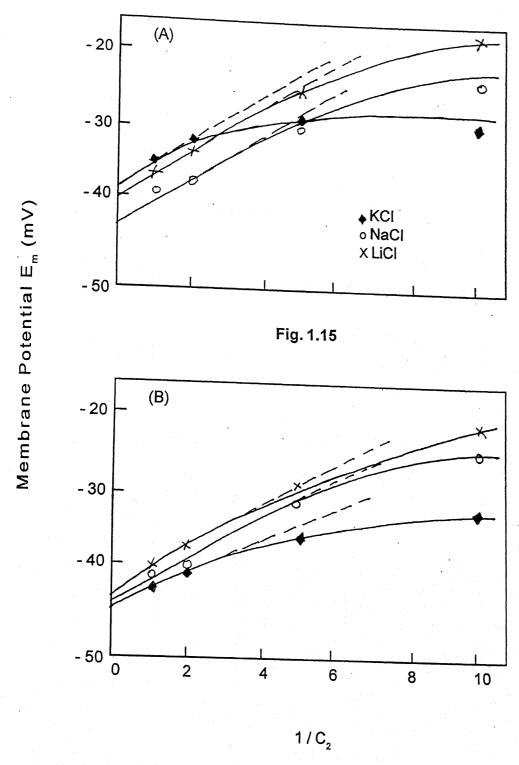


Fig. 1.16

Plots of membrane E_m (mV) against 1/C₂ for polystyrene based (A) cobalt phosphate and (B) nickel phosphate membranes

Table 1.12

Values of the effective fixed charge density ϕ (eq/l) obtained from Kobatake's permselectivity method for various membrane electrolyte system at 25± 0.1°C

Electrolyte	KCl	NaCl	LiCl
Membranes	•		
Cobalt	4.5	3.2	3.2
phosphate			
$(\phi X) \times 10^3$, eq/1			
Nickel phosphate	3.2	3.2	3.2
$(\phi X) \times 10^3$, eq/1			

Table 1.13

Values of the effective fixed charge density ϕx (eq/l) obtained from tasaka's method for various membrane electolyte system at 25± 0.1° C

Electrolyte	KCl	NaCl	LiCl
Membranes			
Cobalt	1.1	1.7	2.0
phosphate			
$(\phi X) \times 10^3$, eq/1			
Nickel phosphate	1.1	2.0	2.2
$(\phi X) \times 10^3, \text{ eq}/1$			

location of energy peaks and wells and also by comparing the heights of energy barriers (i.e., the difference between outer wells and peaks). It has been found that the larger ion encounters bigger entrance barrier lying very close to the surface of the membrane. The entrance barrier for the smaller ion is not only to lesser height but also lies a farther in (39). The location of the outermost well has been assumed to be the same for all the species, while that of the inner well is much farther in for the smaller ion than the larger ones. Keeping in mind these facts, it can be argued that the magnitude of the above mention activation parameters should be higher for larger ions that for smaller ones.

The magnitude of ΔS^{\neq} indicates the mechanism of flow, and has been interpreted in a number of ways. The low negative values of ΔS^{\neq} fount for ion permeation through the polystyrene based membrane used in the present investigation are attributable to electrolyte diffusion with partial immobilization in the membrane, the partial immobility increasing with the increase of density of charge on the permeant. This conclusion is in good agreement with the most recent finding of Marcus (73), who established that the translational immobilization entropy of solvents follows the sequence.

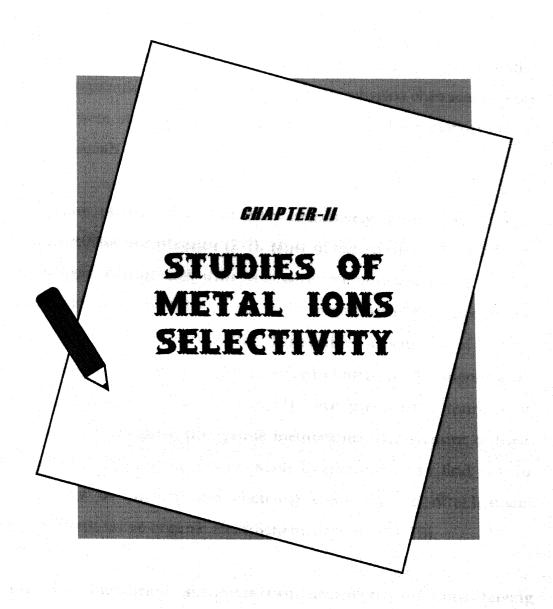
 $Li^+ > Na^+ > K^+$

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Studies of Metal Ions Selectivity

Introduction

Transport phenomena through membranes in biological systems as well as in many industrial processes, are important because of their potential use in various separation processes. Studies on the physico chemical aspects of membranes were started a few decades ago. An, excellent monograph by Lakshminarayanaiah covers progress in this field (1).

Membrane phenomena have been extensively studied with both natural and artificial membranes (2-7). Most of the studies with artificial membranes were carried out with polymeric membranes systems and there seems to be very little work with membranes prepared from inorganic gets probably because of the complexities arising out of factors such as mechanical stability, conformational change in the membrane. matrix, etc. Siddiqi and coworkers (8-11) have prepared a number of polystyrene based inorganic precipitate membranes. On account of their stability and ion exchanging power, such membranes may find use in many processes of nuclear and chemical technology, electrochemical engineering, preparative organic electrochemistry, etc (12,13).

When a membrane separates two electrolytic solutions having different concentrations, the mobile species penetrate the membrane and various transport phenomena are induced in the system. (14). The total electric potential difference observed under zero current flow between two aqueous solutions separated by a membrane has been one of the most

widely characterized electrochemical and bioelectric phenomena (15-22). The fixed charge concept of Teorell (23) and Meyer and Sievers (24) for the charged membranes is a pertinent starting point for the investigation of actual mechanisms of ionic or molecular processes, which occur in the membrane phase. For biological membranes the electrical potential difference is usually described in terms of the Goldman- Hodgkin-Katz (25, 26) equation, whereas for certain ion exchange membranes permeable solely to species of one sign, it is described by a generalized Nernst equation. Both the Goldman-Hodgkin-Katz and the Nernst equations contain ionic permeability ratio terms. Depending on the transport mechanism, or the assumptions made in the derivation, the permeability ratio has been given various physical meaning as: mobility ratio (27) ion exchange equilibrium constant (28, 29) the product of the mobility ratio and the Donnan ratio (23, 24), the product of the mobility ratio and the distribution coefficient ratio (26), the product of the mobility ratio and ion exchange equilibrium constant (16) or the product of equivalent conductance ratio and the ratio of partition coefficient (2). Sandblom et al. (15,16) and Eisenman (30) have discussed the significance and implications of the observed permeability ratio. Recently a number of reviews (31-33) dealing the ion selectivity of membrane have been appeared.

The main purpose of the present work is to apply the recently developed membrane theories to the measurements of membrane potentials, bi-ionic and multi-ionic potentials and membrane conductance. These theories have been used for the evaluation of thermodynamically effective fixed charge density, permeability ratio of cations using conductivity measurements and potentiometric selectivity

constant for the polystyrene based nickel and cobalt phosphate membranes.

The theory of absolute reaction rates has also been utilized for the evaluation of Arrhenius activation energy (Ea), and the change of enthalpy (ΔH^*) , entropy (ΔS^*) and free energy (ΔF^*) of activation by making use of conductance data observed for membranes in contact with various monovalent electrolytes. On the basis of the magnitude of these thermodynamic activation parameters, the selective membrane behavior has also discussed in the light of an advanced theory of membrane selectivity (34).

Experimental

Polystyrene-based membranes of nickel and cobalt phosphate are prepared as described earlier in the Chapter I. The membranes thus prepared were washed with deionized water to remove free electrolytes. The bionic and multi-ionic potentials measured across freshly prepared polystyrene based nickel and cobalt phosphate membranes by constructing an electrochemical cell of the following type and using a Pye-precision vernier potentiometer.

Reference	Electrolyte	Membrane	Electrolyte	Reference
Electrode	Solution (i)	Memorane	Solution (ii)	Electrode

The reference electrodes used were reversible saturated calomel electrodes (Hg/Hg2Cl2) connected to the solution via KCl-agar bridges. Membrane potentials were measured by maintaining a tenfold difference

in the electrolyte concentrations. The bi-ionic potential (BIP) measurement were carried out either by keeping the concentration of both the electrolytes same on the two sides of the membrane, or by maintaining the concentration of one of the electrolytes constant and changing that of the other multi-ionic potential were measured on the lines suggested by Lakshminarayanaiah (1).

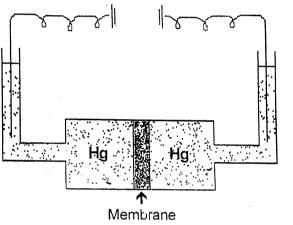
For the measurement of electrical conductivity, membrane was first dipped and equilibrated in an appropriate electrolyte solution. It was then clamped between two half cells and measurements were made according to Fig. 2.1 using a conductivity bridge (Cambridge Instrument Co. Ltd., England). All measurement was carried out at 25±0.1°C. The error in measurement of membrane potential was within ±0.1% whereas electrical conductivity could be measured to better than 0.05%.

Results and Discussion

The value of membrane potential observed experimentally across both the inorganic precipitate polystyrene based nickel and cobalt phosphate membrane by taking dilute solution sides positive are given in Tables 2.1 and 2.2 respectively. The variations of membrane potential with the change of electrolyte concentrations for various 1:1 electrolytes are shown in Figs. 2.2 and 2.3. In both the figures it has been found that membrane potential values decrease with the increase of electrolyte concentration and on the basis of these potential values the membranes follow the sequence of the selectivity of metal ions:

 $K^+ > Na^+ > Li^+$

Conductivity Bridge



Pt. Electrode

Fig. 2.1

Cell for measuring the electrical conductivity of membrane

Table 2.1

The values of the observed membrane potential E_m (mV) across polystyrene based nickel phosphate membrane at $25\pm0.1^{\circ}C$

Electrolyte Concentration/mol 1-1 C / C	KCl	NaCl	LiCl
$1 \times 10^{-1} / 1 \times 10^{-2}$	-42.3	-40.3	-40.4
$5x10^{-2}/5x10^{-3}$	-40.2	-40.2	-37.0
$1x10^{-2}/1x10^{-3}$	-31.9	-24.4	-21.4
$5x10^{-3}/5x10^{-4}$	-14.0	-12.0	-6.8
$1 \times 10^{-3} / 1 \times 10^{-4}$	1.4	8.00	4.4
$5x10^{-4}/5x10^{-5}$	10.2	10.1	8.0
$1 \times 10^{-4} / 1 \times 10^{-5}$	12.4	12.4	15.2

Table 2.2

The values of the observed membrane potential E_m (mV) across polystyrene based cobalt phosphate membrane at 25±0.1°C

Electrolyte Concentration/mol I^{-1} $C_{\parallel}/C_{\parallel}$	KCI	NaCl	LiC1
$1 \times 10^{-1} / 1 \times 10^{-2}$	-34.2	-38.6	-34.9
$5x10^{-2}/5x10^{-3}$	-31.3	-36.7	-32.5
$1 \times 10^{-2} / 1 \times 10^{-3}$	-28.4	-21.6	-16.3
$5x10^{-3}/5x10^{-4}$	-10.4	-14.4	-10.3
$1 \times 10^{-3} / 1 \times 10^{-4}$	1.4	-4.9	5.1
$5x10^{-4}/5x10^{-5}$	8.9	10.1	15.4
$1 \times 10^{-4} / 1 \times 10^{-5}$	9.8	14.5	19.5

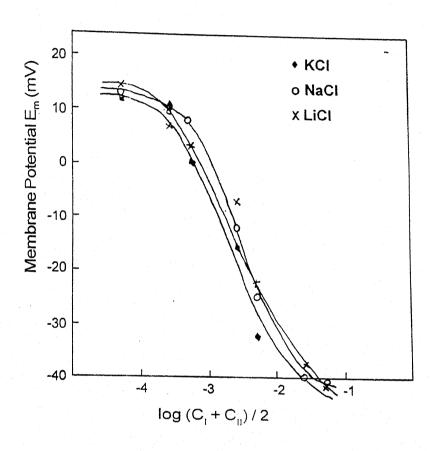


Fig. 2.2

Plots of membrane potential E_m (mV) against $\log{(C_{\|}+C_{\|})}/2$ using 1:1 electrolytes across polystyrene based nickel phosphate membrane.

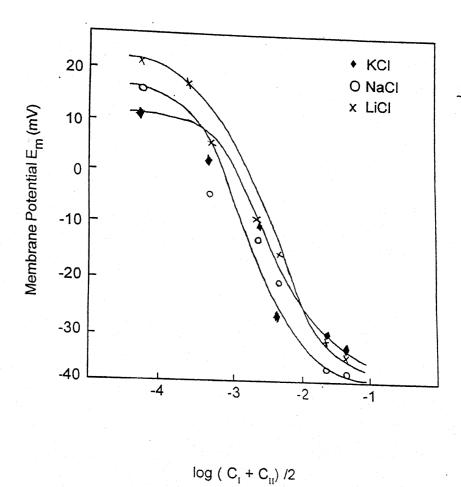


Fig. 2.3

Plots of membrane potential E_m (mV) against $\log (C_{\parallel} + C_{\parallel})/2$ using 1:1 electrolytes across polystyrene based cobalt phosphate membrane.

In the absence of a pressure or temperature gradient, the generation of a steady e.m.f. between two solutions of an electrolyte of different concentrations separated by a membrane, can be attributed to the presence of net charge on the membranes. Such charges play an important role in the sorption and transport of simple electrolytes in artificial as well as natural membranes (35-44) and impart some important electrochemical properties of coions, counter ions and neutral molecules. Hence, for detailed investigation of membrane selectivity, its thermodynamically effective fixed charge density is to be determined. It can be evaluated by making the use of an equation derived on the basis of thermodynamics of irreversible processes. This approach employs a phenomenological coefficient to correlate the gradients that exist across a membrane and their resulting fluxes.

Kobatake and coworkers (45,46) integrated the basic flow equations, provided by thermodynamics of irreversible processes to derive the following equation for the degree of perm selectivity (Ps) of the membrane electrolyte system by taking into consideration an ionizable membrane in contact with solutions of monovalent electrolyte of concentrations C_{\parallel} and C_{\parallel} ($C_{\parallel} > C_{\parallel}$).

$$P_s = \frac{1 - t_{app} - \alpha}{\alpha - (2\alpha - 1)(1 - t_{app})} = \frac{1}{(4\xi^2 + 1)^{\frac{1}{2}}}$$
(2.1)

Where α, ξ and tapp are membrane parameter, i.e., fraction of ionic mobility ratio, relative concentration and the apparent transference number of coions in membrane phase. Further, these can be expressed as:

$$\alpha = u_+^0 / (u_+^0 + u_-^0) \tag{2.2}$$

$$\xi = C/\phi X \tag{2.3}$$

$$E_{\rm m} = -(RT/F) (1-2t_{\rm app}) \ln C_{\parallel}/C_{\parallel}$$
 (2.4)

When the average external salt concentration, $C = (C_{\parallel} + C_{\parallel})/2$, is high in comparison with the thermodynamically effective fixed charge density ϕX , i.e., $\xi >> 1$, the membrane potential can be expressed as

$$E_{m} = -(RT/F) (2\alpha - 1) \ln C_{\parallel}/C_{\parallel}$$
 (2.5)

On the other hand, when the salt concentration is very low, the membrane potential expression becomes.

$$-E_{\rm m} = -(RT/F) \ln C_{\parallel}/C_{\parallel}$$
 (2.6)

If the membrane potential follows the eq. (2.6), the membrane may be referred as a perfectly perm selective, where t_{app} becomes Zero and Ps tends to unity. On the other hand, when membrane potential follows eq. (2.5), t_{app} becomes $(1-\alpha)$ and Ps equal to zero. Hence, it can be said that Ps takes a value between zero and unity depending on the external salt concentration for a given membrane electrolyte pair.

In accordance with eq. (2.1) the straight-line plot of Ps values given in Tables 2.3 and 2.4 of membranes against $(4\xi^2 + 1)^{-1/2}$ are shown in Figs. 2.4 and 2.5 which confirms the applicability of the irreversible

Table 2.3

The values of the perm selectivity Ps of the membrane using various 1:1 electrolytes at different concentration for polystyrene based nickel phosphate membrane

Electrolyte Concentration/mol 1-1 $C_{\parallel}/C_{\parallel}$	KCI	NaCl	LiCl
$1 \times 10^{-1} / 1 \times 10^{-2}$	0.06	0.78	0.83
$5x10^{-2}/5x10^{-3}$	0.65	0.76	0.76
$1 \times 10^{-2} / 1 \times 10^{-3}$	0.51	0.53	0.68
$5x10^{-3}/5x10^{-4}$	0.23	0.38	0.34
$1 \times 10^{-3} / 1 \times 10^{-4}$	-0.11	0.05	0.18
$5x10^{-4}/5x10^{-5}$	-0.17	0.02	0.11
$1 \times 10^{-4} / 1 \times 10^{-5}$	-0.23	-0.14	0.00

Table 2.4

The values of the perm selectivity Ps of the membrane using various 1:1 electrolytes at different concentration for polystyrene based cobalt phosphate membrane

NaCl	LiC1
0.74	0.76
0.70	0.71
0.62	0.48
0.41	0.43
0.30	0.18
-0.02	0.00
-0.06	0.10
	-0.06

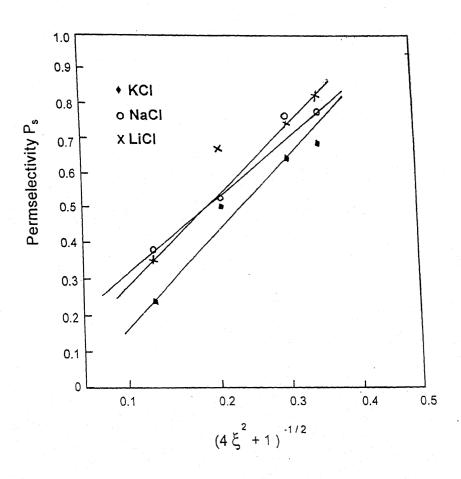
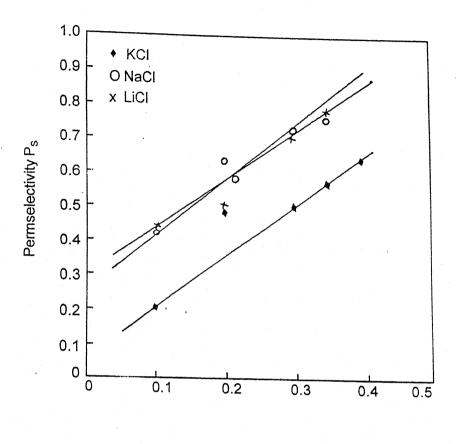


Fig. 2.4 Plots of permselectivity P $_s$ Vs log $(4\xi^2+1)^{-1/2}$ for polystyrene based nickel phosphate membrane



 $\log (4\xi^2 + 1)^{-1/2}$

Fig. 2.5

Plots of permselectivity P_s Vs $\log{(4\xi^2+1)}^{-1/2}$ for polystyrene based cobalt phosphate membrane.

thermodynamic approach to our model system. When the average concentration C, and the thermodynamically effective fixed charge density ϕX , are of the same magnitude, ξ becomes equal to unity and Ps equal to $1/\sqrt{5}$. The magnitude of concentration corresponding to this value of Ps is a measure of ϕX .

Another expression, which is useful for the evaluation of magnitude ϕX , has been proposed by Tasaka et al (47). These authors derived an equation for membrane potential taking some assumptions into account for low and high concentration limit of electrolyte solutions.

Another theory developed by Tasaka and coworkers (47) has also been used in the evaluation of magnitude of ϕX . In the absence of an externally applied electric field or a pressure gradient at the limit of low electrolyte concentration (where the effect of flow of water is negligible), the expression for membrane potential can be written:

$$-E_m = \frac{RT}{F} \ln \frac{C_{\parallel}}{C_{\parallel}} \tag{2.7}$$

Whereas at the limit of high electrolyte concentration we have:

$$-E_m = \frac{RT}{F} \left(\frac{\gamma - 1}{\gamma} \right) \left(\frac{\phi X}{2} \right) 1/C_{\parallel} \tag{2.8}$$

Which predicts a linear relationship between E_m and $1/C_1$ and allows the evolution of ϕX from the slop of straight lines obtained by plotting E_m against $1/C_1$.

The effective fixed charge density ϕX , has also been related to E_m and t_a (34).

$$(F/RT)E_m = -\ln \gamma + \ln \frac{-\phi X + \sqrt{(\phi X)^2 + 4C_{\parallel}^2}}{-\phi X + \sqrt{(\phi X)^2 + 4C_{\parallel}^2}}$$

$$+(2t_{-}-1)\ln\left[\frac{(1-2t_{-})\phi X}{1-2t_{-})\phi X} + \frac{\sqrt{(\phi X)^{2}+4C_{\parallel}^{2}}}{\sqrt{(\phi X)^{2}+4C_{\parallel}^{2}}}\right]$$
(2.9)

Which can be approximated to eq. (2.10) if the membrane is slightly charged.

$$(F/RT) E_m = (2t_- - 1) \ln \gamma + \frac{2(\gamma - 1)}{\gamma} t. (1 - t_-) \frac{\phi X}{C_\parallel}$$
 (2.10)

This equation predicts a straight-line plot of (F/RT) E_m vs. $1/C_1$ at fixed γ , and allows the evaluations of t_- and ϕX from the intercept and slope of the liner plot.

Equation (2.1), (2.8) and (2.10) have been utilized to calculate the effective fixed charge density values (ϕX) and the values of transference number (t_-), which are given in Tables 2.5 to 2.8. The values of transference number t_- are plotted against log $1/C_{\parallel}$, as shown in Figs. 2.6 and 2.7. The plots of Ps versus log ($C_{\parallel}+C_{\parallel}$)/2 are shown in Figs. 2.8 and 2.9, Em vs. $1/C_{\parallel}$ are shown in Figs. 2.10 and 2.11 and (F/RT) Em vs. $1/C_{\parallel}$ are shown in Figs. 2.12 and 2.13. As the values of ϕX are quite low, the membranes used in this investigation is expected to have low

Table 2.5

The values of effective fixed charge density of polystyrene based nickel phosphate membrane using 1:1 electrolytes derived from different theories

Electrolyte	KCl	NaCl	LiC1
Kobatake & cowarkers	1.9x10 ⁻³	4.7x10 ⁻³	4.2x10 ⁻³
Nagasawa et al.	1.1x10 ⁻³	1.75x10 ⁻³	2.05x10 ⁻³
Aizawa et al.	1.2x10 ⁻³	1.75x10 ⁻³	2.05x10 ⁻³

Table 2.6

The values of effective fixed charge density of polystyrene based cobalt phosphate membrane using 1:1 electrolytes derived from different theories

Electrolyte	KCl	NaCl	LiCl
Kobatake & cowarkers	5.3x10 ⁻³	2.5x10 ⁻³	3.7x10 ⁻³
Nagasawa et al.	1.1x10 ⁻³	1.7x10 ⁻³	$2.0x10^{-3}$
Aizawa et al.	1.7x10 ⁻³	1.3x10 ⁻³	1.8x10 ⁻³

Table 2.7

Transference number t_ coions derived from observed membrane potential at various electrolyte concentrations through polystyrene based nickel phosphate membrane

Electrolyte Concentration/mol 1^{-1} $C_{\parallel}/C_{\parallel}$	KCl	NaCl	LiCl
$1x10^{-1}/1x10^{-2}$	0.84	0.84	0.83
$5x10^{-2}/5x10^{-3}$	0.82	0.83	0.81
$1x10^{-2}/1x10^{-3}$	0.75	0.69	0.76
$5x10^{-3}/5x10^{-4}$	0.61	0.59	0.54
$1 \times 10^{-3} / 1 \times 10^{-4}$	0.47	0.42	0.46
$5x10^{-4}/5x10^{-5}$	0.41	0.41	0.42
$1 \times 10^{-4} / 1 \times 10^{-5}$	0.34	0.34	0.36

Table 2.8

Transference number t_ coions derived from observed membrane potential at various electrolyte concentrations through polystyrene based cobalt phosphate membrane

Electrolyte	KCl	NaC1	LiCl
Concentration/mol 1^{-1} $C_{\parallel}/C_{\parallel}$			
$1 \times 10^{-1} / 1 \times 10^{-2}$	0.77	0.81	0.80
$5x10^{-2}/5x10^{-3}$	0.74	0.79	0.76
$1 \times 10^{-2} / 1 \times 10^{-3}$	0.73	0.67	0.62
$5x10^{-3}/5x10^{-4}$	0.60	0.61	0.57
$1 \times 10^{-3} / 1 \times 10^{-4}$	0.68	0.53	0.44
$5x10^{-4}/5x10^{-5}$	0.42	0.41	0.37
$1 \times 10^{-4} / 1 \times 10^{-5}$	0.48	0.37	0.32

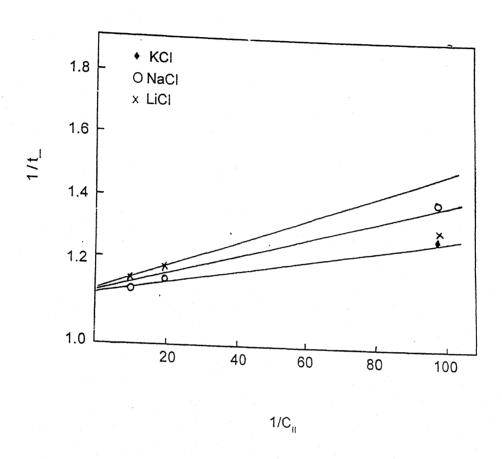


Fig. 2.6

Plots of transference number (t_) against $1/C_{\parallel}$ of various 1:1 electrolytes at different concentration across polystyrene based nickel phosphate membrane.

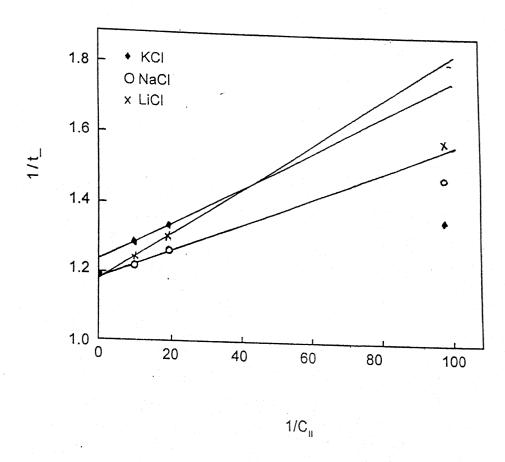


Fig. 2.7

Plots of transference number (t_) against $1/C_{\parallel}$ of various 1:1 electrolytes at different concentration across polystyrene based cobalt phosphate membrane.

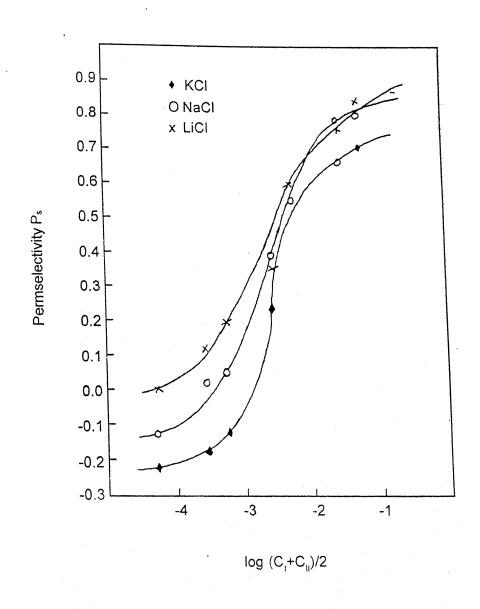


Fig. 2.8 Plots of permselectivity P $_{\!s}$ Vs log (C $_{\!\parallel}$ +C $_{\!\parallel}$)/2 for polystyrene based nickel phosphate membrane

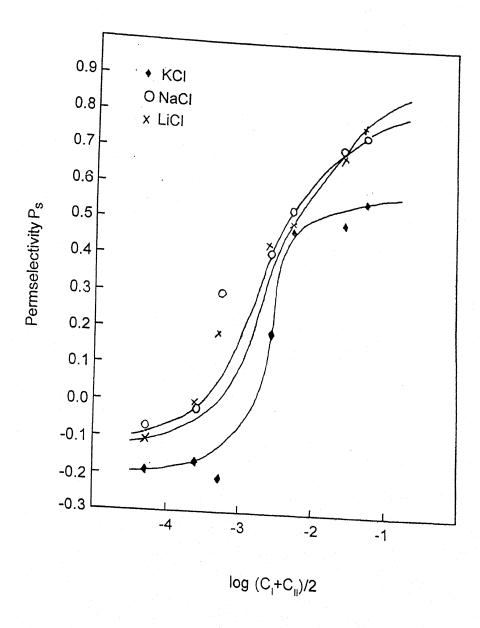


Fig. 2.9

Plots of permselectivity P_s Vs log $(C_1+C_2)/2$ for polystyrene based cobalt phosphate membrane.

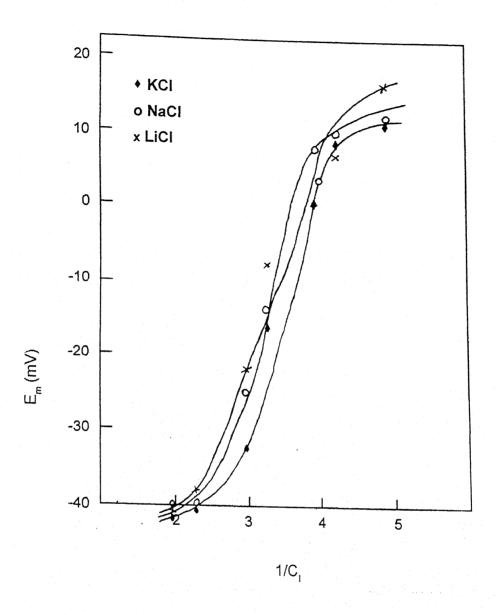


Fig. 2.10 $Plots \ of \ membrane \ potential \ E_{_m} \ (mV) \ Vs. \ 1/C_{_l} \ for \ polystyrene \ based \ nickel \ phosphate \ membrane$

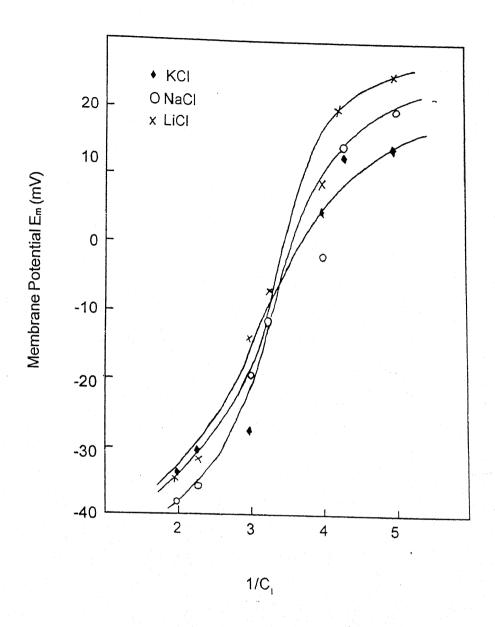


Fig. 2.11

Plots of membrane potential E_m (mV) Vs. 1/C_I for polystyrene based cobalt phosphate membrane

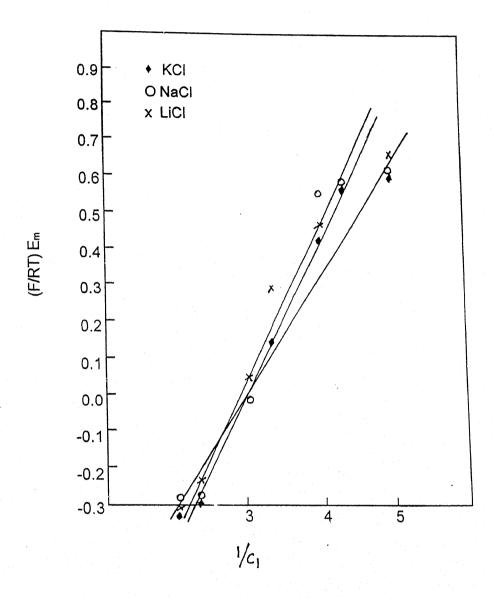


Fig. 2.12

Plots of (F/RT) E_m (mV) Vs. $1/C_l$ for polystyrene based nickel phosphate membrane

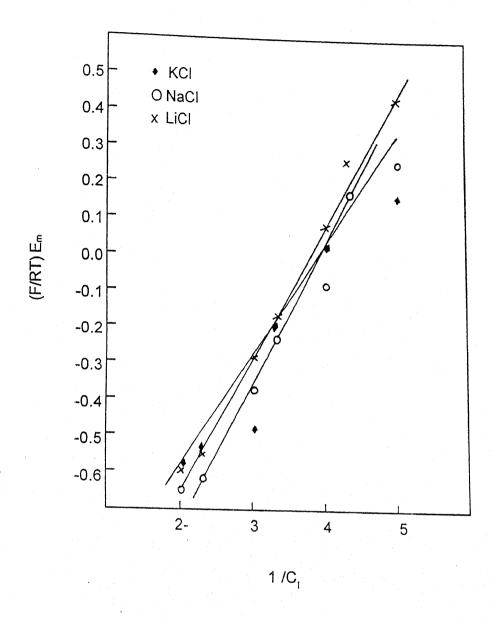


Fig. 2.13 $Plots \ of \ (F/RT) \ E_{m} \ (mV) \ Vs. \ 1/C_{l} \ for \ polystyrene \ based \ cobalt \ phosphate \ membrane$

negative electrostatic field strength of the fixed charge sites. For such a situation following the Eisenman and Horn (40). selectivity sequence of metal ions in the membrane phase was proposed as:

$$K^+ > Na^+ > Li^+$$

The same sequence has also already been studied by Eisenman and Horn (40) which strength to our work.

The selectivity sequence of nickel and cobalt phosphate membrane for the ions of the same sign can be confirmed by various experimental methods. Some of the most widely used methods, such as:

1. Bi-ionic Potential

The steady e.m.f. of a bionic cell, containing two electrolytes of the type ix and jx (or ix and iY) separated by a membrane, is called the biionic potential (BIP) [48], which is a measure of the selectivity of the
membrane for ions of the same sign. The BIP has been considered by
Helfferich (29) in accordance with the concepts of the TMS theory (22,23),
as being the algebraic sum of two interfacial potentials and an internal
diffusion potential. A complete mathematical discussion under conditions
: (a) membrane diffusion control, (b) film diffusion contorl, and (c)
coupled membrane film diffusion control has been presented (28). For a
general case involving complete membrane diffusion control, the BIP for
counter ions is given by

$$E = \frac{RT}{ZF} \ln \frac{\overline{D}_i}{\overline{D}_j} \frac{a_j^i}{a_j^i} \frac{\overline{V}_j}{\overline{V}_i} \frac{K_i}{K_j} = \frac{RT}{ZF} \ln \left[K_{ji} \left(\frac{\overline{D}_i}{\overline{D}_j} \frac{a_i^i}{a_j^i} \frac{\overline{V}_j}{\overline{V}_i} \right) \right]$$
 (2.11)

Where a_i/a_j , $\overline{D}_i/\overline{D}_j$, $\overline{V}_i/\overline{V}_j$ are the ratio of the activities, diffusion coefficients and the activity coefficients of the counter ions i and j respectively. Overbars refers the phenomena in the membrane phase; R,T,Z and F have their usual meanings. Using the Einstein's relation Di= UiRT and the generalized Nernst equation in which the permeability ratio are independent of the external electrolyte solutions (27,49) the eq. (2.11) reduces to the form.

$$E = \frac{RT}{ZF} \ln \left[\frac{a_i' \overline{U}_i}{a_i'' \overline{U}_i} k_{ij} \right] = \frac{RT}{ZF} \ln \left[\frac{a_i' \overline{p}_i}{a_i'' \overline{P}_i} \right]$$
(2.12)

eq. (2.12) gives

$$\overline{P}_i / \overline{P}_j = K_{ji} \overline{U}_i / \overline{U}_j$$

This equation has also been derived most recently by Sandbolm and Eisenman (30) from the thermodynamic treatment for fixed site membranes which implies that the permeability ratio is, quite generally, related to the ion exchange equilibrium constant K_{ji} and the ratio of mobilities of the critical ions. Further, using the well known relation.

$$\overline{U}_i/\overline{U}_j = \overline{\lambda_i}/\overline{\lambda}_j \tag{2.13}$$

eq. (2.13) gives.

$$\overline{P}_{i}/\overline{P}_{j} = K_{ji} \overline{U}_{i}/\overline{U}_{j} = K_{ji} \overline{\lambda}_{i}/\overline{\lambda}$$
(2.14)

Where $\overline{\lambda}_i$ is the conductivity of the membrane when it is wholly in i form and $\overline{\lambda}_j$ is the conductivity of the membrane when it is wholly in the j form.

The quantity $\overline{P}_i/\overline{P}_j$ is considered truly a membrane property (17). It is independent of the changes made in the activities as and as of the external solution. Thus it is apparent from eq. (2.12) that a plot of log as against potential for a constant as should give a straight line. Similarly a straight line should be obtained if as is varied and as is kept constant. Both these lines should show potential changes of RT/F or 59.2 mV at 25°C for each tenfold change in activity when membranes are separating 1:1 electrolytes. Accordingly BIP values across polystyrene based nickel cobalt phosphate membranes were determined for various electrolyte pairs, viz., KCl-NaCl, KCl-LiCl and NaCl-LiCl, taking the concentration (0.01M) of one of the electrolyte constant and varying the concentration of the other electrolyte between 0.001 M to 0.01 M. In second set of experiment the concentration of the other electrolyte was kept constant and the concentration of the first electrolyte was varied in same range. The bi-ionic potentials thus observed were plotted against logarithm of t he mean molal activity. Two sets of straight lines in accordance with the expectation of eq. (2.12) are obtained as shown in Figs. 2.14 and 2.15. The straight lines confirm the views of Nicolsky (28) and Eisenman (30) that the permeability ratios are independent of external solution conditions. In order to derive the values of the permeability ratio, these straight lines were extended to cut the activity axis at zero potential. Thus two sets of ai and aj values for which potential E was zero were obtained. At zero potential the ratio ai/aj was equal to $\overline{P}_i/\overline{P}_j$. The values

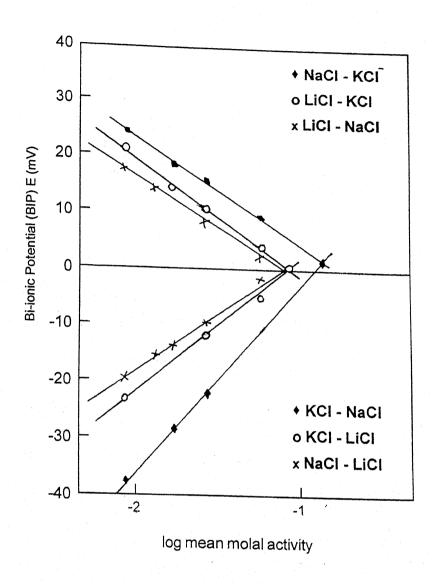
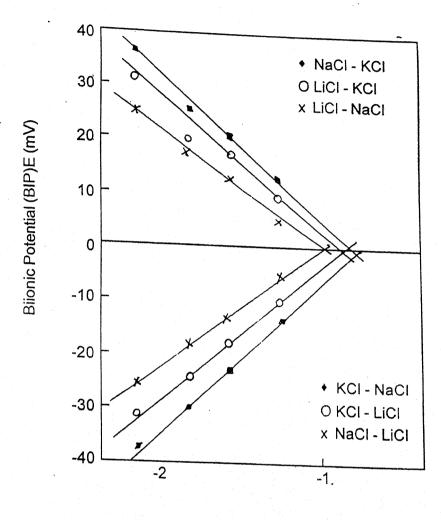


Fig. 2.14

Plots of bi-ionic potential (BIP) E (mV) Vs. logarithm of mean molal activity for polystyrene based nickel phosphate membrane



log mean molal activity

Fig. 2.15

Plots of bi-ionic potential (BIP) E (mV) Vs. logarithm of mean molal activity for polystyrene based cobalt phosphate membrane.

of $\overline{P}_i/\overline{P}_j$ derived in this way for nickel and cobalt phosphate membranes and different electrolyte pairs are as follows:

$$\overline{P}_{k^+}/\overline{P}_{Na^+} = 1.72, \quad \overline{P}_{k^+}/\overline{P}_{Li^+} = 1.50, \quad \overline{P}_{Na^+}/\overline{P}_{Li^+} = 1.36.$$

The values of $\overline{P}_i/\overline{P}_j$ are generally low which point towards the fact that the membranes are relatively more imbibed in equilibrium water content (37). The value of intramembrane permeability ratio also refer to the selectivity sequence of the membrane for the cations as follows:

$$K^+ > Na^+ > Li^+$$

This order of selectivity (50) on the basis of the Eisenmean-Sherry model of membrane selectivity (51-53) point towards the weak field strength of the charge groups attached to the membrane matrix. This is in accordance with charge density (charge density≈10⁻³ mol 1⁻¹) determinations membranes (17).

Interposing the membrane between two different electrolyte solutions at the same concentration also carried out bi-ionic potential measurements. The BIP values were low when the membrane was used to separate concentrated electrolyte solutions whereas it increased with decreasing salt concentrations. In this way experimentally observed values of BIP across both the membranes are given in Tables 2.9 to 2.10 and this change is depicted in Figs. 2.16 and 2.17. The permeability ratio $\overline{P}_i/\overline{P}_j$ calculated from BIP values using eq. (2.12) given in Tables 2.11 and 2.12, were also seen concentration dependent. The variation in BIP

Table 2.9

Experimental values of bi-ionic potential (BIP) E (mV) across polystyrene based nickel phosphate membrane at $25\pm0.1^{\circ}\text{C}$

Electrolyte Concentration/mol 1^{-1} $C_{\parallel}/C_{\parallel}$	KCl-NaCl	KCl-LiCl	NaCl-LiCl
$1 \times 10^{-1} / 1 \times 10^{-1}$	2.26	-3.94	-3.26
$5x10^{-2}/5x10^{-2}$	4.54	-2.73	-2.03
$1 \times 10^{-2} / 1 \times 10^{-2}$	8.56	2.60	2.24
$5x10^{-3}/5x10^{-3}$	11.65	3.44	4.15
$1 \times 10^{-3} / 1 \times 10^{-3}$	19.84	16.46	13.46

Table 2.10

Experimental values of bi-ionic potential (BIP) E (mV) across polystyrene based cobalt phosphate membrane at $25\pm0.1^{\circ}\text{C}$

Electrolyte Concentration/mol 1-1	KCl-NaCl	KC1-LiC1	NaCl-LiCl
$C_{\parallel}/C_{\parallel}$			
$1 \times 10^{-1} / 1 \times 10^{-1}$	2.40	-4.51	-4.20
$5x10^{-2}/5x10^{-2}$	2.54	-2.45	-2.45
$1x10^{-2}/1x10^{-2}$	6.81	2.61	1.99
$5x10^{-3}/5x10^{-3}$	13.31	5.10	3.44
$1x10^{-3}/1x10^{-3}$	14.79	18.51	9.75

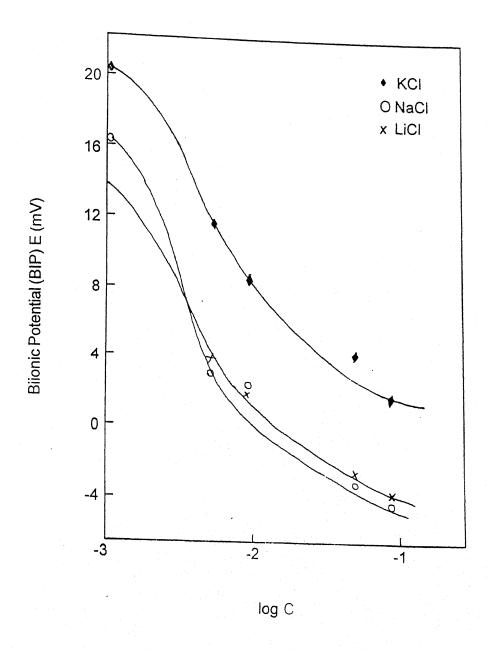


Fig. 2.16

Plots of bi-ionic potential (BIP) E (mV) Vs. logarithm C for polystyrene based nickel phosphate membrane

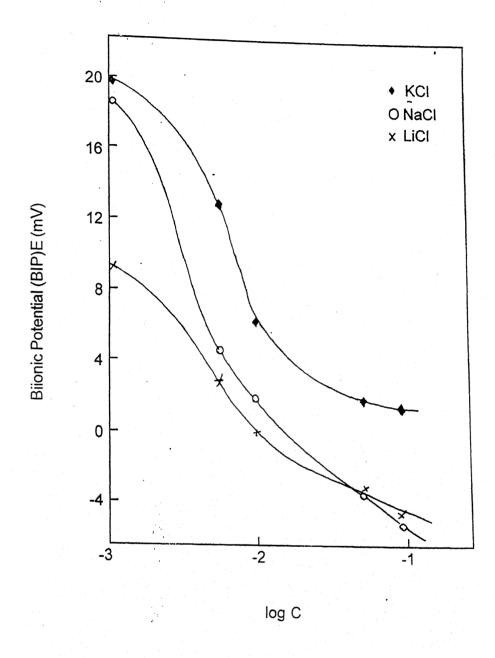


Fig. 2.17

Plots of bi-ionic potential (BIP) E (mV) Vs. logarithm C for polystyrene based cobalt phosphate membrane

Table 2.11

Values of the intramembrane permeability ratio $(\overline{P}_i/\overline{P}_j)$ of various 1:1 electrolyte ion pairs for polystyrene based nickel phosphate membrane

Electrolyte				
	KCl-NaCl	KCl-LiCl	NaCl-LiCl	
Concentration/mol 1-1	$\overline{P}_{\!k}^{+}$ / $\overline{P}_{\!\scriptscriptstyle N\!lpha}^{+}$	$\overline{P}_{k}^{+}/\overline{P}_{U}^{+}$	$\overline{P}_{Na}^{+}/\overline{P}_{Ii}^{+}$	
$C_{\parallel}/C_{\parallel}$	Na Na	1 k / Li	P_{Na}/P_{Li}	
$1x10^{-1}/1x10^{-1}$	1.08	0.84		
$5x10^{-2}/5x10^{-2}$		0.64	0.87	
	1.19	0.91	0.91	
$1 \times 10^{-2} / 1 \times 10^{-2}$	1.43	1.08	1.08	
$5x10^{-3}/5x10^{-3}$	1.56	1.13	1.18	
$1 \times 10^{-3} / 1 \times 10^{-3}$	2.16	1.85	1.67	

Table 2.12

Values of the intramembrane permeability ratio $(\overline{P}_i/\overline{P}_j)$ of various 1:1 electrolyte ion pairs for polystyrene based cobalt phosphate membrane

Electrolyte ion pair	KCl-NaCl	KCl-LiCl	NaCl-LiCl
Concentration/mol 1-1	$\overline{P}_{k}^{+}/\overline{P}_{Na}^{+}$	$\overline{P}_{\!\scriptscriptstyle k}^{+}/\overline{P}_{\!\scriptscriptstyle Li}^{+}$	$\overline{P}_{Na}^{+}/\overline{P}_{Li}^{+}$
$C_{\parallel}/C_{\parallel}$		n Li	- Na , - Li
$1x10^{-1}/1x10^{-1}$	1.23	0.91	0.91
$5x10^{-2}/5x10^{-2}$	1.29	1.11	1.03
$1 \times 10^{-2} / 1 \times 10^{-2}$	1.67	1.21	1.13
$5x10^{-3}/5x10^{-3}$	2.17	1.44	1.45
$1 \times 10^{-3} / 1 \times 10^{-3}$			1.10

caused by the change produced in the permeability ratio may be ascribed due to structural changes produced at the membrane solution interfaces. polystyrene based inorganic precipitated membranes exchangeable groups as part of its structure which may account for its negative charge. The exchangeable cations will be free to move in the pores. Within the pores there will be a diffused ionic atmosphere from the charged wall. Since the membrane under investigation carries low ionic charge densities (i.e., charge density of the order 1X10⁻³ mol l⁻¹), anion encroachment into membrane seems to be the most probable phenomenon. The thickness of the atmosphere depends upon the electrolyte concentration. In very dilute solution of electrolyte, the thickness of anions becomes so great that only cations are present in the pores and the membrane becomes impermeable to anions, which is actually a condition necessary for the derivation of eq. (2.12) with constant permeability ratio. Thus the best data on $\overline{P}_i/\overline{P}_j$ are that from the dilute solutions. It may therefore, be concluded that the existence of an expression for E with constant permeability ratio cannot be characteristic of all the membrane is permeable only to species of one sign. This is in agreement with the mathematical treatment advanced by Sandblom and Eisenman (16).

In order to have knowledge of selectivity K_{ij} from the predetermined values of $\overline{P}_i/\overline{P}_j$ the ratio of electrical conductivities $\overline{\lambda}_i/\overline{\lambda}_j$ as demanded by eq. (2.14) must be known. Membrane conductance measurements were carried out when it was wholly in the from i or wholly in the form j. The values of membrane conductance at various electrolyte concentrations of both the membranes are given is Tables 2.13 and 2.14 which are relatively more dependent upon the concentration of the

Table 2.13

Observed values of membrane conductance (Sm $^{-1}$) for monovalent electrolyte at $25\pm0.1^{\circ}\text{C}$ across polystyrene based nickel phosphate membrane

Electrolyte	KCl-NaCl	KCI-LiC1	NaCl-LiCl
Concentration/mol 1-1			
C_{\parallel} / C_{\parallel}			
$1 \times 10^{-1} / 1 \times 10^{-1}$	0.90	0.51	0.34
$5x10^{-2}/5x10^{-2}$	1.5	1.01	0.81
$1x10^{-2}/1x10^{-2}$	3.5	2.5	2.2
$5x10^{-3}/5x10^{-3}$	3.9	3.1	2.7
$1 \times 10^{-3} / 1 \times 10^{-3}$	7.9	7.1	6.7

Table 2.14

Observed values of membrane conductance (Sm $^{-1}$) for monovalent electrolyte at $25\pm0.1^{\circ}$ C across polystyrene based cobalt phosphate membrane

Electrolyte	KCl-NaCl	KCl-LiCl	NaCl-LiCl
Concentration/mol 1-1			
$C_{\parallel}/C_{\parallel}$			
$1x10^{-1}/1x10^{-1}$	0.63	0.61	0.40
$5x10^{-2}/5x10^{-2}$	1.03	1.01	0.71
$1 \times 10^{-2} / 1 \times 10^{-2}$	3.5	3.4	2.3
$5x10^{-3}/5x10^{-3}$	4.5	4.5	3.1
$1 \times 10^{-3} / 1 \times 10^{-3}$	8.1	7.7	5.1

electrolyte. Within the membranes as shown in Figs 2.18 and 2.19. This implies that the membrane has a relatively high Donnan uptake of anion and a low selectivity constant value. This is in agreement with the findings of Heymann and Rabinov (54). Spiegler et al. (55) and our own findings with ion exchange membrane (4-8). The values of selectivity, Kij evaluated from the ratio of electrical conductivities $\overline{\lambda}_i/\overline{\lambda}_j$ and the intramembrane permeability ratio $\overline{P}_i/\overline{P}_j$ using eq. (2.14) are given in Tables 2.15 and 2.16.

2. Mixture Method

To assess the selectivity sequence of the membrane for the cations, values of potentiometric selectivity constants K_{ij}^{Pot} have been evaluated using the methods developed by Dole (56) and modified and improved by Buck et al. (57,58). However, a number of methods (59) have been suggested for the determination of selectivity constant by taking the mixtures of electrolytes across the membrane and measuring the electric potentials developed. The general equation (eq. 2.15) for membrane potential E in an electrochemical cell of the type

has often been used to derive the value of K_{ij}^{Pot} of membrane electrolyte systems.

$$E = \frac{nRT}{F} \ln \left[(a'_i)^{l/n} + (K_{ij}^{Pot} a'_j)^{l/n} \right] / \left[(a''_j)^{l/n} \right] + \left[(K_{ij}^{Pot} a''_j)^{l/n} \right]$$
 (2.15)

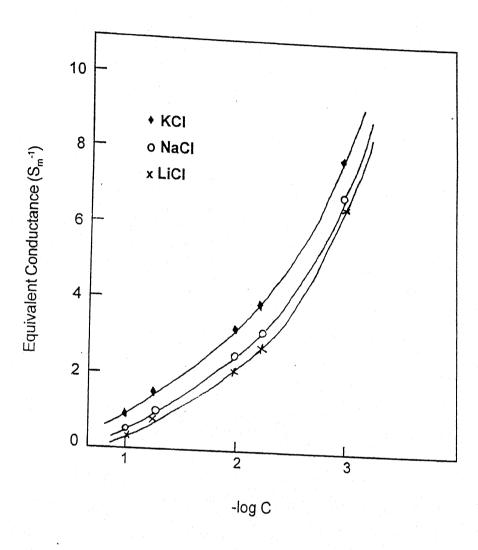


Fig. 2.18

Typical plots of equivalent conductance $(S_{\mathfrak{m}}^{-1})$ Vs. -log C for polystyrene based nickel phosphate membrane.

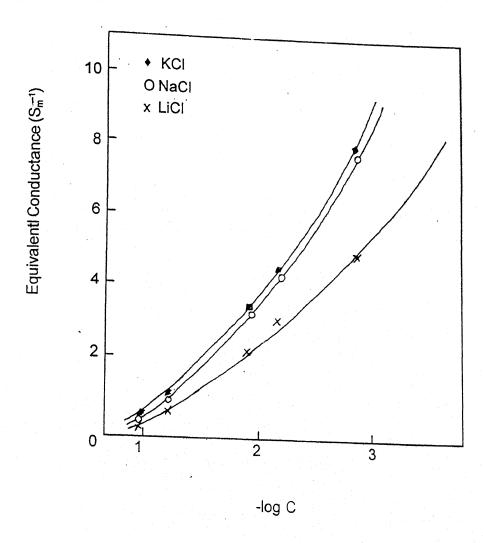


Fig. 2.19

Typical plots of equivalent conductance $(S_{\mathfrak{m}}^{\text{-1}})$ Vs. -log C for polystyrene based cobalt phosphate membrane.

Table 2.15

Values of the selectivity K_{ji} derived from intramembrane permeability ratio and the ratio of electrical conductivities at various electrolyte for polystyrene based nickel phosphate membrane

Selectivity	V		:
Concentration/mol 1-1	$\mathbf{K}_{\mathtt{Nak}}$	K _{Lik}	KLina
$1 \times 10^{-1} / 1 \times 10^{-1}$	0.61	0.33	0.50
$5x10^{-2}/5x10^{-2}$	0.73	0.33	0.50
$1 \times 10^{-2} / 1 \times 10^{-2}$	1.11	0.45	0.75
$5x10^{-3}/5x10^{-3}$	1.24	0.71	0.92
$1 \times 10^{-3} / 1 \times 10^{-3}$	1.81	1.42	0.98 1.51

Table 2.16

Values of the selectivity K_{ji} derived from intramembrane permeability ratio and the ratio of electrical conductivities at various electrolyte for polystyrene based nickel phosphate membrane

Selectivity	K _{Nak}	KLik	K _{LiNa}
Concentration/mol 1-1			
$1x10^{-1}/1x10^{-1}$	1.05	0.52	0.55
$5x10^{-2}/5x10^{-2}$	1.21	0.62	0.66
$1x10^{-2}/1x10^{-2}$	1.24	0.72	0.71
$5x10^{-3}/5x10^{-3}$	1.59	0.86	1.02
$1 \times 10^{-3} / 1 \times 10^{-3}$	2.06	1.32	1.03

Where

$$K_{ij}^{Pot} = K_{ij} (U_i/U_j)^{1/n}$$

If n=1 and the concentrations on side (") are held constant then eq. (2.15) gives

E = const + (RT/F) ln
$$[a'_j + (K_{ij}^{Pot} a'_j)]$$
 (2.16)

Equation (2.16) is considered a normal form for ideal behavior of ion selective electrode responsive to species i and j if the response for cation is more positive for solution of species i than for j at equal activities then K_{ij}^{Pot} is less than unity and the electrode is more sensitive to i than to j (34). equation (2.16) has been used in various ways for the evaluation of potention metric selectivity constants K_{ij}^{Pot} . Various aspects of eq (2.16) for the evaluation of K_{ij}^{Pot} have been reviewed by Lakshminarayanaiah (59). Mixture methods based on eq. (2.16) were first developed and used extensively by Lengyel and Blum (60) and later by Eisenman (61). Srinivasan and Rechnitz (62) examined several methods for the determination of K_{ij}^{Poi} , while Pungor and Toth (63,64) strongly recommended another form of the mixture method is the titeatiov method of the Dole (56), which was modified and improved by Buck et al (34, 57). This method provides extensive sets of mixture response potentials ΔE_{ij} were measured and the selectivity coefficient were calculated using the equation (2.17).

ln
$$K_{ij}^{Pot}$$
 (apparent) = ln $\{\exp[(\Delta E_{ij} - E_i)/S)] - \ln(a_j/a_i)\}$ (2.17)

Where S is the slope of the pure at response curve as shown in Figs. 2.20 and 2.21.

Electrical potential ΔE_{ij} across both polystyrene based membranes in the electrochemical cell of the type shown above were measured by taking fixed concentrations of both the primary ions (i.e. i and j) on the side ("), where as in another experiment only one ion either i or j on the side (") at different concentration was taken and electrical potential ΔE_i or ΔE_j were plotted against log ai or log aj as shown in Figs. 2.20 and 2.21. Parallel lines depicted in figures were obtained which indicates the ideal behavior of the membrane systems. The slope S of the line was used to derive the value of K_{ij}^{Pot} (apparent) using eq. (2.17). In this way, the values of K_{ij}^{Pot} obtained for both the polystyrene based nickel and cobalt phosphate membranes using various 1:1 electrolytes are given in Tables 2.17 and 2.18.

Polystyrene based nickel and cobalt phosphate membranes with various 1:1 electrolytes were assumed as homogeneous membrane elements which contains charged rigid capillary structure or gels having a diameter large as compared to the thickness of the electrical double layer at the walls (23,24,28) in accordance with classical fixed charge theory of Teorell (23), Meyer and Sievers (24), Sollner (65). Gregor (66). Schmid (67). Kobatake and coworkers (68-71) and Tasaka and coworkers (47) etc. Flow of electrolyte by diffusion because of the presence of a net charge on the membrane gives rise to membrane potential which regulates the flow of electrolyte by increasing the speed of the slow moving ions and also by decreasing the speed of the fast moving ion. The electrical double layer at the membrane solution interface seems to control the ion permeation as suggested by Tien and Ting (72) for bilayer

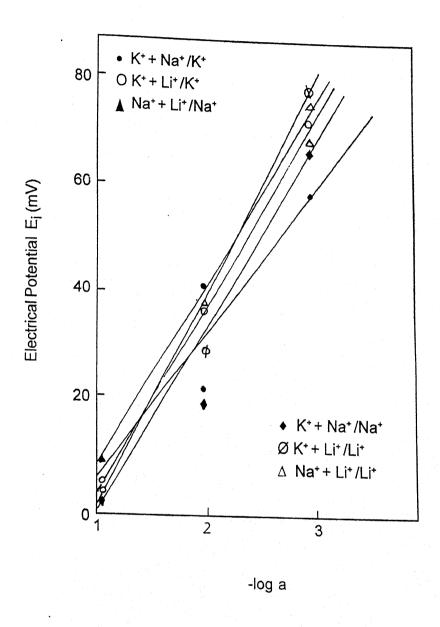


Fig. 2.20

Plots of electrical potential E_i (mV) Vs. -log a for polystyrene based nickel phosphate membrane

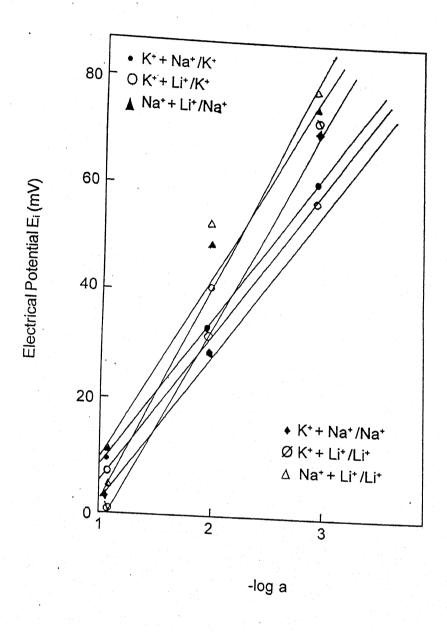


Fig. 2,21

Plots of Electrical potential E_i (mV) Vs. -log a for polystyrene based cobalt phosphate membrane

Table 2.17

Values of potentiometric selectivity constant (K_{ij}^{Pot}) for the polystyrene based nickel phosphate membrane at various electrolyte concentration

Selectivity	K _{K-Na}	K _{K-Li}	K _{Na-Li}
Concentration/mol 1-1			
C_{\parallel} / C_{\parallel}			
1x10 ⁻¹	0.63	0.35	0.40
1x10 ⁻²	1.11	1.21	0.48 1.33
1x10 ⁻³	4.00	5.21	2.17

Table 2.18

Values of potentiometric selectivity constant (K_{ij}^{Pot}) for the polystyrene based cobalt phosphate membrane at various electrolyte concentration

Selectivity constant	K _{K-Na}	K _{K-Li}	K _{Na-Li}
Concentration/mol 1-1			
1x10 ⁻¹	0.81	0.48	0.61
1×10^{-2}	1.11	1.21	1.41
1×10^{-3}	3.51	4.02	3.21

membranes and our own findings with inorganic precipitate nickel phosphate membrane. Perfect Donnan exclusion of coions was realized in the dilute limit of the external solution and the selectivity sequence of the membrane for alkali metal ions was

 $K^{+} > Na^{+} > Li^{+}$

Selectivity of Membranes in Energetic Terms

In order to substantiate our findings and further to understand the selectivity of membranes in energetic terms, the values of various activation parameters have been evaluated on the basis of the rate theory. The need for the use of rate theory has been felt because electrical measurements carried out for assessing selectivity involve kinetic contributions to the permeation process and their explanation cannot be expected to be given rigorously in terms of equilibrium energetic concepts. The rate theory describes any processes from diffusion to chemical reaction in terms of elementary jumps over energy barrier and can be used to represent the processes of permeation in as much detail or with as much accuracy as desired. The Permit encounters energy maxima (barriers) and minima (wells) represent the energies of the transition state and diffusion past these unfavorable loci can be represented by single jumps over the corresponding barrier. The progress over each barrier is proportional to the number of ions attaining the energy needed. The rate constant Ki, for crossing over a barrier is related to standard Gibb's free energy of activation, ΔF^{*} , by :

$$K_i = A_i \exp\left(-\Delta F^*/RT\right) \tag{2.18}$$

Where Ai is the frequency of attempted hops. The (ΔF^*) is related to enthalpy (ΔH^*) and entropy (ΔS^*) of activation.

$$\Delta F^{\neq} = \Delta H^{\neq} - T \Delta S^{\neq} \tag{2.19}$$

 ΔH^{\neq} and ΔS^{\neq} can be evaluated with the help of specific conductance, π , by making the use of the following relationship.

$$\pi = RT / Nh \exp \left(-\Delta H^{+} / RT\right) \exp \left(\Delta S^{+} / R\right)$$
(2.20)

The obtained values of ΔH^* can be used to evaluate the Arrhenius activation energy, E_a on the basic of the equation.

$$E_a = \Delta H^{\neq} + RT \tag{2.21}$$

To use equation (2.20) $\log \pi nH/RT$ has been plotted against 1/T as shown in Figs. 2.22 and 2.23. The straight-line plots confirm line plots confirm the applicability of this equation to our model system and allow the calculation of ΔH^{\pm} and ΔS^{\pm} from the slope and intercept of the linear plots. The parameters so evaluated have been used to calculate the magnitude of ΔF^{\pm} and E_{a} with the help eqs. (2.19) and (2.20) respectively. The results of these calculations are summarized in Tables 2.19 and 2.20.

The size dependence of the magnitude of E_a , ΔF^* and ΔH^* shows that a larger ion has more difficulty in crossing the membrane than a smaller one. This type of variation can be explained by considering the

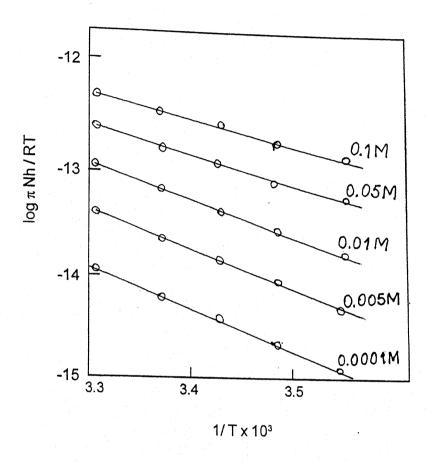


Fig. 2.22

Plots of log μ Nh/RT Vs 1/T for polystyrene based nickel phosphate membrane

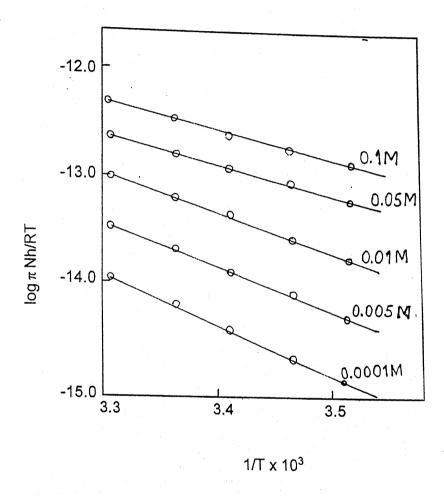


Fig. 2.23

Plots of log μ Nh/RT Vs 1/T for polystyrene based cobalt phosphate membrane.

Table 2.19

The value of thermodynamic activation parameters evaluated of the basis of theory of absolute reaction rates

Membrane		Nickel	Phosphate		
Electrolyte			- поэрпасс		
	Concentration	Ea	Δ F ≠	∆H [≠]	∆S [≠]
	$1x10^{-1}$	1.30	10.80	1.32	14.30
	5x10 ⁻²	2.10	13.65	2.75	15.21
KC1	1x10 ⁻²	4.11	15.92	3.90	16.70
	$5x10^{-3}$	5.65	17.10	5.25	17.50
	1x10 ⁻³	7.10	18.75	6.50	20.70
	1x10 ⁻¹	1.13	11.8	1.11	19.20
	$5x10^{-2}$	2.94	13.27	2.17	19.82
NaCl	$1x10^{-2}$	4.17	15.22	3.32	20.16
	$5x10^{-3}$	5.35	17.23	4.97	21.37
	1x10 ⁻³	6.94	18.24	6.23	23.13
	$1x10^{-1}$	1.01	11.60	1.01	20.0
	5x10 ⁻²	2.91	11.13	2.73	21.32
LiCl	$1x10^{-2}$	4.13	15.53	3.50	22.75
	$5x10^{-3}$	5.23	17.14	4.75	23.35
	1x10 ⁻³	6.17	17.43	9.97	24.25

Table 2.20

The value of thermodynamic activation parameters evaluated of the basis of theory of absolute reaction rates

Membrane		Cobalt	Phosphate		er (d. meren er
Electrolyte			r moshuace		
	Concentration	Ea	∆F ≠	ΔH [≠]	∆S *
	1x10 ⁻¹	1.50	11.0	1.37	14.0
	5x10 ⁻²	2.40	13.72	2.81	15.14
KC1	$1x10^{-2}$	4.15	15.98	3.96	16.63
	$5x10^{-3}$	5.71	17.23	5.32	17.08
	1x10 ⁻³	7.40	18.82	6.80	20.63
	1x10 ⁻¹	1.21	11.3	1.16	17.5
	$5x10^{-2}$	2.98	13.32	2.25	18.22
NaCl	1x10 ⁻²	4.23	15.41	3.42	19.34
	$5x10^{-3}$	5.41	17.36	4.13	20.45
	1x10 ⁻³	6.70	18.27	6.10	21.37
	$1x10^{-1}$	1.01	11.80	1.07	20.00
	5x10 ⁻²	2.98	11.80	1.07 2.84	20.20 21.41
LiCl	$1x10^{-2}$	4.27	15.67	3.76	22.87
	$5x10^{-3}$	5.63	17.28	4.88	23.52
	1x10 ⁻³	6.38	18.83	9.96	24.45

location of energy peaks and wells and also by comparing the heights of energy barriers (i.e., the difference between outer wells and peaks). It has been found that the larger ion encounters bigger entrance barrier lying very close to the surface of the membrane. The entrance barrier for the smaller ion is not only to lesser height but also lies a farther in (39). The location of the outermost well has been assumed to be the same for all the species, while that of the inner well is much farther in for the smaller ion than the larger ones. Keeping in mind these facts, it can be argued that the magnitude of the above mention activation parameters should be higher for larger ions that for smaller ones.

The magnitude of ΔS^{\neq} indicates the mechanism of flow, and has been interpreted in a number of ways. The low negative values of ΔS^{\neq} fount for ion permeation through the polystyrene based membrane used in the present investigation are attributable to electrolyte diffusion with partial immobilization in the membrane, the partial immobility increasing with the increase of density of charge on the permeant. This conclusion is in good agreement with the most recent finding of Marcus (73), who established that the translational immobilization entropy of solvents follows the sequence.

 $Li^+ > Na^+ > K^+$

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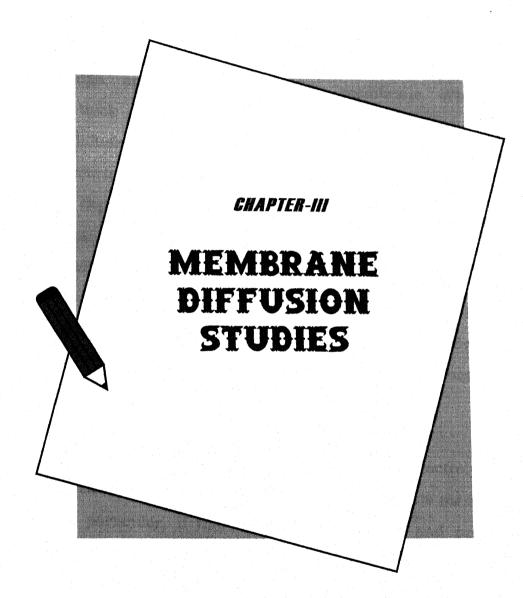
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Membrane Diffusion Studies

Introduction

Generally describing steady-state membrane processes are based on a step vias mechanism for the migrating substance of sorption into, diffusion through, and desorption from the membrane. When the membrane is thick enough, the over-all rate of the process will be governed by diffusion alone, a condition which simplifies theoretical treatment. Unfortunately, however, diffusivities may be strongly concentration dependent: the swelling of the membrane facilitates diffusion. Several different mathematical relations have been proposed to express diffusivity as a function of concentration, and elaborate and excellent measurements are being made of concentration profiles in membranes during permeation. However, conventional steady state permeation and equilibrium sorption data contain enough information for the same purpose (1).

When two solutions of different concentrations of an electrolyte are placed on both sides of a membrane, we can observe various membrane phenomena. In particular, if there are no temperature and pressure differences across the membrane and also if no electric field is applied, the permeation velocities of water and ions through the membrane as well as the electrostatic potential difference appearing on both sides of the membrane (membrane potential) may be our subjects for research. These membrane phenomena have been extensively studied by many investigators. From those studies, it is now well established that there is

a strong interaction between fluxes of water and ions through a charged membrane. So called anomalous osmosis is caused by the interaction between both fluxes. The permeation velocities of ions and the membrane potential must also be affected by the flow of water (2-7).

A variety of compounds and associated processes that have been employed to prepare them and the important literature concerning transport phenomena are described (8-17). A theoretical discussion of many of the transport phenomena has been given in a monograph by schlogl (15). On the other side the polystyrene based membrane in a system with high water content and neglectable concentration of fixed ions. Precipitation membranes act as ion selective barriers and display rectification of electrical current. Their special properties can be explained by the adsorption theory of precipitation membranes (2). Some other membrane processes are under development at the moment, for instance, facilitated Transport by liquid and fixed site carrier membranes. Carrier-facilitated Transport can also be determined by diffusion only, which depends for example on the kind of membrane applied. Furthermore, the technique of controlled release of drugs from (biodegradable) reservoirs is a process that is mainly determined by diffusion. Therefore, Transport processes occurring across membranes are of great interest for biologists, who use them as simple models for physiological membranes in order to understand the behavior of complex cell membranes in terms of established physicochemical principles. It was demonstrated by Teorell (18) that the gastric mucosal membrane, in some formal aspects at least, behaved exactly like parchment membrane. His further findings, that electrolytic transport processes in stomach could be handled by some thing similar to Fick's diffusion law and that Nernst-Planck formulae for electrical potential were applicable, has encouraged us to proceed further with the studies of parchment supported membranes (19-26) as model for biological systems.

In this chapter, the diffusion rate studies of simple metal ions through polystyrene based nickel and cobalt phosphate membranes under isothermal conditions are described. The diffusion rate of the ions have been computed using a simple cell assembly shown in Fig. 3.1. The advantage of the method is that various membrane parameters namely, membrane resistance Rm, membrane potential Em and the computed diffusion rate could be known within two –three minutes. The method is based on an equation derived by W.W. Kittelberger (27) from the simple laws of electrolysis. The results have been discussed in the light of Eisenman-sherry model of membrane selectivity (28-31) and the theory of absolute reaction rates (31-33).

Experimental

Polystyrene based nickel and cobalt phosphate membranes were prepared as described earlier in chapter-I

The membranes thus prepared were washed with deionized water to remove free electrolytes. It was then clamped between two half cells as shown in Fig. 3.1 the half cells contained 125 ml. of electrolyte solution while the capacity of each of the cell holding the membrane was about 130 ml. Initially these concentrations C_1 and C_2 were 0.001 M and 0.1M. Each of the half cell was fitted with a conductivity cell (λ_1 and λ_2) firmly fixed to follow concentration changes using conductivity bridge

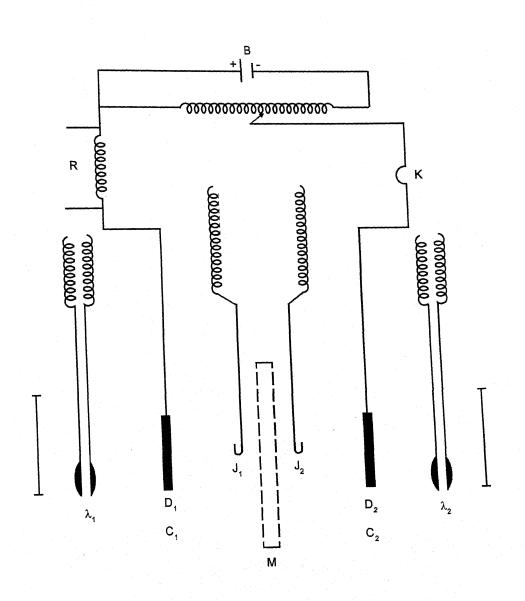


Fig. 3.1
Assembly

(Cambridge Instrument Co. England No. 350140) and two anion reversible Ag-AgCl electrodes – one a disc type (D1, D2) to pass a small d.c. current and another J- shaped wire electrode (J1, J2) to measure membrane potential following current flow. The solutions in both the half cells were kept well stirred by magnetic stirrers. The whole cell assembly was immersed in a water thermostat maintained at 10°C, 15°C, 20°C and 25°C (± 0.1°C).

Exactly known weights or volumes of two test solutions were introduced (say at zero time), and the platinized platinum electrodes were connected to the conductance bridges to follow conductance change with time. No appreciable change in conductance was noted within the 4 hr. period on the C_2 side (0.1M) and so we have assumed this concentration to be practically constant and followed only the conductance change on the C_1 side. The exact concentration of this solution was determined from a calibration curve where conductance was plotted against concentration. Another set of calibration curves were also needed to obtain concentration potential E_2 from the plots of emf against log fc, according to the equation

$$E_{\xi} = \frac{RT}{Z_{+}F} \ln fc \tag{3.1}$$

Using a pair of saturated solomel and Ag-AgCl electrodes in the test solutions on either side of the membrane. For all the electrolytes under investigation $F_{\mathbf{c}}$ was taken as the difference between emf value of the dilute and the concentrated solutions.

Membrane resistance was determined by measuring potential across J₁ and J₂ electrodes with and without applying an external e.m.f to the disc electrodes. The change in potential was taken as IR. The current I passed through the membrane system was determined by measuring IR drop across a precision Kilo-ohm resistor. The current was kept very low in order to minimize the ion transfer during the period (2-3 min.) required for each resistance measurements. The direction of current flow was reversed in each successive measurements.

Membrane potentials were evaluated from the electrical potential developed across J_1 and J_2 electrodes when no current was being passed. The total potential E_{obs} developed across J-shaped Ag/AgCl electrodes (J_1 and J_2) is the algebraic sum of electrode potential $E_{\bar{e}}$ and membrane potential E_m . $E_{\bar{e}}$ was calculated by the equation

$$E_{\bar{c}} = \frac{RT}{Z_{-}F} In \frac{a_2}{a_1} \tag{3.2}$$

and Em was obtained by subtraction.

The thickness of the membranes were as follows:

- 1. Cobalt phosphate membrane = 0.025 cm
- 2. Nickel Phosphate membrane = 0.026 cm

Results and Discussion

Transport phenomena are often described by some extended form of the Nernst-planck flux equation (34). Evaluation of flow requires

integration of these equations under suitable boundary conditions. Some time ago, based on the simple laws of electrolysis, Kittelberger (27) developed the following equation for the migration of ions through a barrier

$$\frac{dQ}{dt} = \frac{1}{Z_{+}FR_{m}} \left[\frac{RT}{Z_{+}F} \ln \frac{a_{2}}{a_{1}} - E_{m} \right] \left[(\frac{Z_{-}}{Z_{+} + Z_{-}}) (\frac{E_{m}}{\frac{RT}{Z_{+}F} \ln \frac{a_{2}}{a_{1}}}) + (\frac{Z_{+}}{Z_{+} + Z_{-}}) \right]$$
(3.3)

Where at and at are activities of the two solutions of an electrolyte on either side of the membrane, Q is the number of milliequivalents of ions diffusing in time t seconds, E_m is the membrane concentration potential, R_m is the electrolyte resistance of the membrane in ohms, Z_+ , Z_- are the valancy of cation and anion respectively, T_- is the absolute temperature, R_- is the gas constant, and F_- is the Faraday constant. Equation (3.3) was used to give the rate dQ/dt at which various electrolytes diffuse through a membrane. For electrolytes (1:1), eq. (3.3) simplifies to

$$\frac{dQ}{dt} = \frac{1}{2FR_m} \left[E_E - E_m \right] \left[\left(\frac{E_m}{E_E} + 1 \right) \right] \tag{3.4}$$

For (2:1) electrolytes eq. (3.3) gives

$$\frac{dQ}{dt} = \frac{1}{3FR_m} \left[\left(\frac{E_{\pm}}{2} - E_m \right) \right] \left(\frac{E_m}{E_{\pm}} + 1 \right)$$
(3.5)

and for electrolytes of the type (3:1) it becomes

Table 3.1

Values of parameters for the diffusion of KCl (0.1m/0.001m) through Polystyrene based cobalt phosphate membrane at $10\pm0.1^{\circ}\text{C}$

Time (hr)	Conc. (C ₁) (M) x 10 ⁴	E _{obs}	Et	Em	R _m	dQ/dt x10 ⁷
	10.9	49.0	74.9	-55.1	666.5	0.58
0.9	11.4	49.0	73.9	-54.9	666.5	0.60
1.4	11.9	48.5	72.8	-54.3	658.9	0.75
1.9	12.4	48.0	71.5	-53.7	639.9	0.80
2.4	13.9	47.1	70.1	-51.8	609.9	0.83
2.9	14.9	46.4	68.9	-50.8	567.9	
3.4	17.9	45.9	67.9	-47.9	524.9	0.87
3.9	19.9	450		77.9	524.9	0.95
	19.9	45.9	66.9	-43.9	499.9	1.00

Table 3.2

Values of parameters for the diffusion of KCl (0.1m/0.001m) through Polystyrene based cobalt phosphate membrane at $15\pm0.1^{\circ}$ C

Time (hr)	Conc. (C ₁) (M) x 10 ⁴	E _{obs} (mV)	E t (mV)	E _m (mV)	R _m	dQ/dt x10 ⁷ (millimol/S)
0.9	11.9	44.9	95.1	-59.7	563.3	3.4
1.4	13.4	44.5	93.9	-56.7	535.6	3.6
1.9	13.9	44.3	92.7	-55.5	519.9	3.8
2.4	15.9	44.0	91.1	-52.8	519.9	4.3
2.9	17.9	43.9	89.4	-49.9	475.9	4.8
3.4	18.9	43.6	88.4	-49.6	442.2	4.9
3.9	19.9	43.4	87.4	-48.7	439.9	5.1

Table 3.3

Values of parameters for the diffusion of KCl (0.1m/0.001m) through Polystyrene based cobalt phosphate membrane at 20±0.1°C

Time	Conc. (C1)	Eobs	Eŧ	Em	R _m	dQ/dt x10 ⁷ (millimol/S)
(hr)	$(M) \times 10^4$	(m V)	(mV)	(mV)	(ohm)	
0.4	10.4	41.9	98.7	-67.5	377.6	4.0
0.9	10.9	41.7	97.4	-66.5	355.9	4.2
1.4	11.9	41.4	95.9	-65.1	354.9	4.3
1.9	12.9	40.9	95.4	-63.9	332.9	5.1
2.4	14.4	40.6	94.6	-61.3	329.4	5.3
2.9	14.9	40.2	93.2	-59.6	306.9	5.6
3.4	16.9	40.0	91.7	-58.8	286.9	5.9
3.9	18.9	39.9	90.4	-56.7	283.9	5.9

Table 3.4

Values of parameters for the diffusion of KCl (0.1m/0.001m) through Polystyrene based cobalt phosphate membrane at $25\pm0.1^{\circ}C$

Time	Conc. (C ₁)	E _{obs} (mV)	Eŧ	Em	R _m	dQ/dt x10 ⁷ (millimol/S)
(hr)	$(M) \times 10^4$		(mV)	(mV)	(ohm)	
0.4	11.9	40.00	99.4	-68.50	283.3	4.21
0.9	12.4	39.90	97.9	-67.60	267.9	4.70
1.4	12.9	39.60	96.1	-66.60	259.9	4.60
1.9	13.9	39.20	94.9	-64.60	240.9	4.86
2.4	14.9	38.90	93.9	-64.20	242.9	4.88
2.9	16.9	38.60	93.4	-60.90	225.5	5.91
3.4	18.4	38.55	92.1	-57.95	218.9	6.70
3.9	19.9	38.40	90.9	-55.80	214.9	6.71

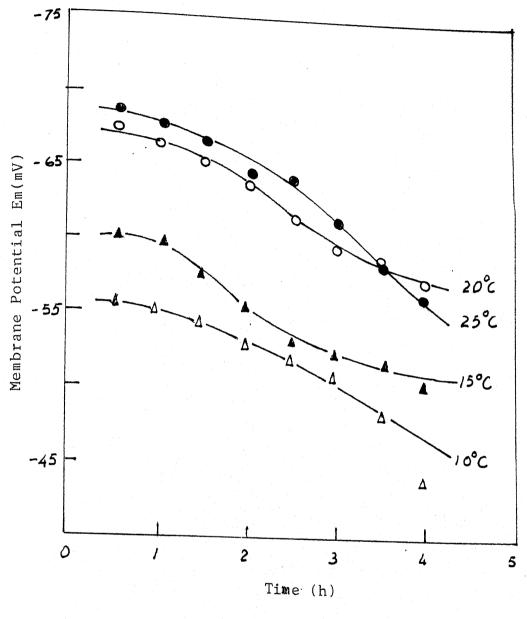


Fig. 3.2

Plots of membrane potential E_m (mV) against Time (h) at different temperatures across polystyrene based cobalt phosphate membrane using KCl electrolyte.

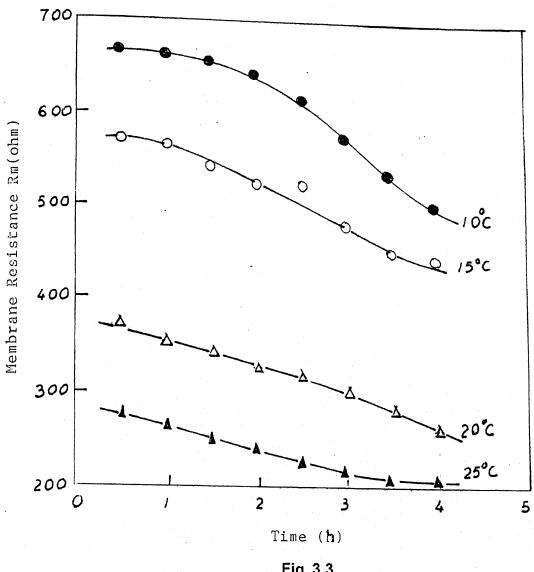


Fig. 3.3

Plots of membrane resistance R_m (ohm) against Time (h) at different temperatures across polystyrene based cobalt phosphate membrane using KCl electrolyte.

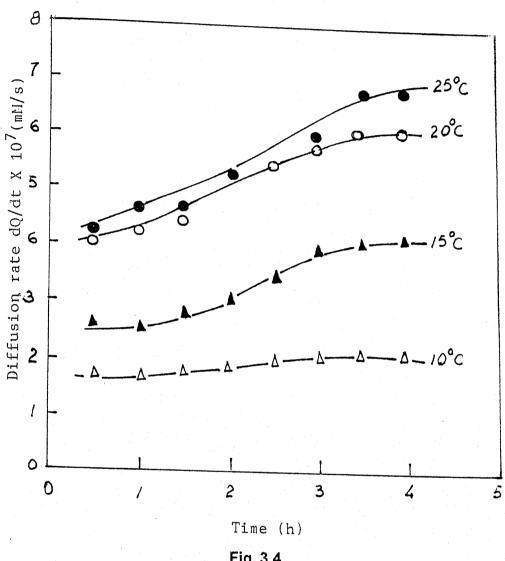


Fig. 3.4

Plots of diffusion rate dQ/dt (mM/s) against Time (h) at different temperatures across polystyrene based cobalt phosphate membrane using KCI electrolyte.

Table 3.5

Values of parameters for the diffusion of NaCl (0.1m/0.001m) through Polystyrene based cobalt phosphate membrane at 10±0.1°C

Time	Conc. (C1)	Eobs	Eŧ			
(hr)	(M) x 10 ⁴	(mV)	(mV)	E _m (mV)	R _m (ohm)	dQ/dt x10 ⁷ (millimol/S)
0.4	11.9	19.4	85.9	-82.9	849.9	0.27
0.9	13.4	18.9	84.7	-81.1	812.4	0.35
1.4	13.9	18.6	83.3	-80.3	787.4	0.48
1.9	15.9	18.3	81.9	-77.5	783.6	0.53
2.4	17.9	17.9	80.6	-75.9	723.5	0.57
2.9	18.4	17.6	79.2	-74.6	702.6	0.66
3.4	19.4	17.4	77.9	-73.7	648.5	0.75
3.9	20.9	17.3	76.9	-71.5	644.9	0.77

Table 3.6

Values of parameters for the Diffusion of NaCl (0.1m/0.001m) through Polystyrene based cobalt phosphate membrane at $15 \pm 0.1^{\circ}$ C

Time	Conc. (C1)	Eobs	Eŧ	Em	Rm	dQ/dt x10 ⁷
(hr)	$(M) \times 10^4$	(mV)	(mV)	(mV)	(ohm)	(millimol/S)
0.4	11.9	17.2	89.9	-87.4	766.5	0.70
0.9	12.4	17.1	88.9	-86.4	710.9	0.72
1.4	13.4	16.9	87.9	-84.9	699.9	1.00
1.9	14.9	16.6	86.9	-82.4	647.6	1.00
2.4	16.4	16.4	85.9	-80.3	627.9	1.10
2.9	17.9	16.0	84.7	-78.4	599.9	1.30
3.4	18.9	15.6	83.4	-77.6	577.5	1.40
3.9	19.9	15.4	82.2	-76.7	534.9	1.60

Table 3.7

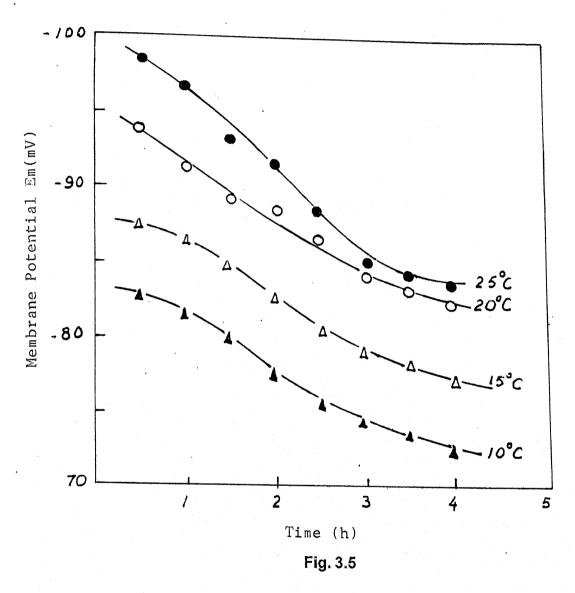
Values of parameters for the diffusion of NaCl (0.1m/0.001m) through Polystyrene based cobalt phosphate membrane at 20±0.1°C

Time	Conc. (C ₁)	Eobs	Et	Em		
(hr)	(M) x 10 ⁴	(mV)	(mV)	(mV)	R _m (ohm)	dQ/dt x10 ⁷ (millimol/S)
0.4	10.9	15.0	97.9	-93.8	586.1	1.2
0.9	11.9	14.9	96.4	-91.0	561.3	1.3
1.4	12.9	14.4	95.1	-88.9	534.3	1.4
1.9	13.9	14.0	93.8	-88.4	499.9	1.6
2.4	14.9	13.9	92.2	-86.8	499.9	1.7
2.9	16.9	13.7	90.9	-84.5	463.5	1.8
3.4	17.9	13.4	89.9	-83.2	453.9	1.9
3.9	18.9	13.1	88.9	-81.8	418.0	1.1

Table 3.8

Values of parameters for the diffusion of NaCl (0.1m/0.001m) through Polystyrene based cobalt phosphate membrane at $25\pm0.1^{\circ}\text{C}$

Time	Conc. (C ₁)	Eobs	Eŧ	Em	R _m	dQ/dt x107
(hr)	$(M) \times 10^4$	(mV)	(mV)	(m V)	(ohm)	(millimol/S)
0.4	10.9	11.6	101.4	-98.4	539.9	1.3
0.9	11.9	11.2	100.1	-96.4	539.9	1.4
1.4	13.9	11.0	98.9	-93.2	499.9	1.5
1.9	14.9	10.9	97.7	-91.5	462.9	1.7
2.4	16.9	10.9	96.2	-88.7	444.3	1.9
2.9	19.9	10.1	95.1	-85.2	419.9	2.1
3.4	20.4	9.9	93.9	-84.3	399.9	2,2
3.9	20.9	9.7	92.9	-83.9	369.9	2.4



Plots of membrane potential E_m (mV) against Time (h) at different temperatures across polystyrene based cobalt phosphate membrane using NaCl electrolyte

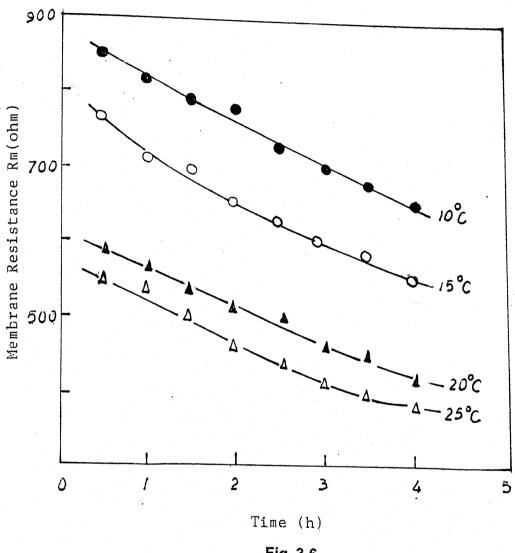
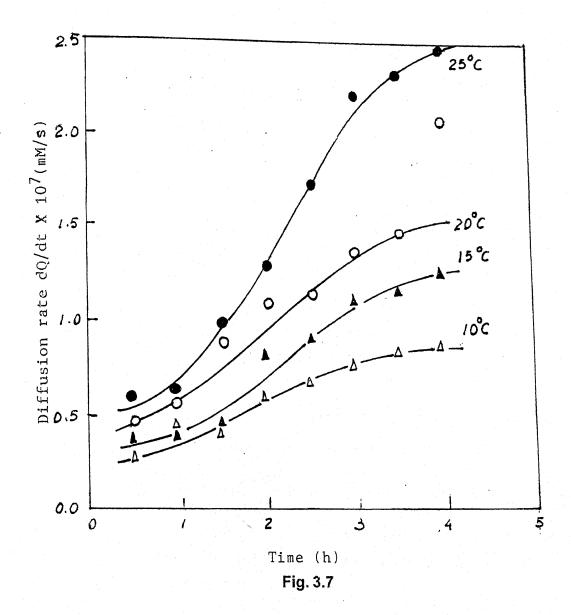


Fig. 3.6

Plots of membrane resistance R_m (ohm) against Time (h) at different temperatures across polystyrene based cobalt phosphate membrane using NaCl electrolyte.



Plots of diffusion rate dQ/dt (mM/s) against Time (h) at different temperatures across polystyrene based cobalt phosphate membrane using NaCl electrolyte.

Table 3.9

Values of parameters for the diffusion of LiCl (0.1m/0.001m) through Polystyrene based cobalt phosphate membrane at $10\pm0.1^{\circ}\text{C}$

Time	Conc. (C1)	Eobs	E _t			
(hr)	(M) x 10 ⁴	(m V)	(mV)	E _m (mV)	R _m (ohm)	dQ/dt x10 ⁷ (millimol/8)
0.4	10.90	15.8	89.9	-89.9	890.9	
0.9	11.7	15.3	88.9	-88.7	880.9	0.01 0.11
1.4	13.4	14.9	87.9	-86.2	849.9	0.11
1.9	14.9	14.4	86.9	-84.0	820.9	0.27
2.4	17.9	13.9	85.9	-79.9	783.9	0.46
2.9	18.9	13.5	84.7	-79.2	779.9	0.60
3.4	19.9	13.1	83.4	-78.5	778.9	0.61
3.9	20.9	12.9	82.2	-77.0	769.9	0.65

Table 3.10

Values of parameters for the diffusion of LiCl (0.1m/0.001m) through Polystyrene based cobalt phosphate membrane at $15\pm0.1^{\circ}$ C

Time	Conc. (C ₁)	Eobs	Eż	Em	Rm	dQ/dt x107
(hr)	$(M) \times 10^4$	(mV)	(m V)	(mV)	(ohm)	(millimol/S)
0.4	9.9	13.2	99.9	-96.7	839.9	0.29
0.9	12.9	12.9	97.9	-90.6	832.9	0.39
1.4	14.9	12.4	96.1	-87.7	773.2	0.49
1.9	15.9	12.0	94.9	-86.4	766.5	0.75
2.4	16.4	11.6	93.9	-86.2	759.9	0.81
2.9	17.9	11.3	92.9	-84.2	749.9	1.00
3.4	19.9	10.9	92.1	-82.4	754.9	1.10
3.9	21.9	10.4	90.9	-80.0	749.9	1.20

Table 3.11

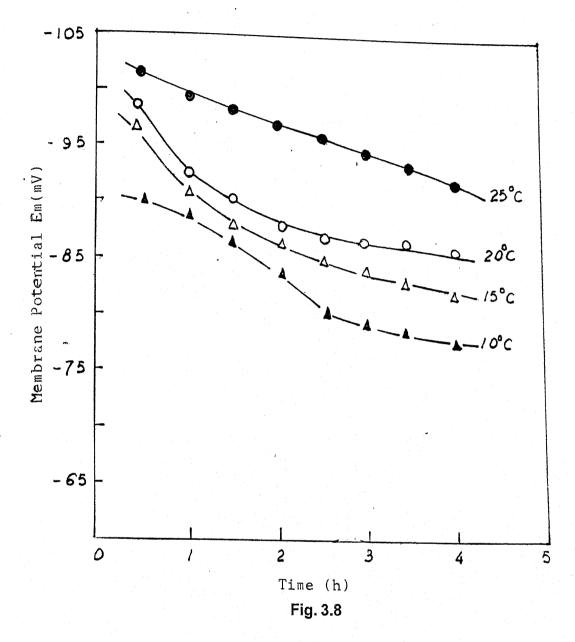
Values of parameters for the diffusion of LiCl (0.1m/0.001m) through Polystyrene based cobalt phosphate membrane at 20±0.1°C

Time	Conc. (C1)	Eobs	Eŧ			
(hr)	(M) x 10 ⁴	(mV)	⊥-₹ (m V)	Em	Rm	dQ/dt x107
0.4	11.9		(-11.4)	(mV)	(ohm)	(millimol/S)
	11.9	10.4	104.9	-99.0	755.4	0.36
0.9	12.9	10.0	103.7	-91.9	742.1	0.47
1.4	13.9	9.7	102.2	-89.9	733.2	0.79
1.9	14.9	9.6	100.9	-87.6	697.5	1.00
2.4	16.4	9.3	99.6	-87.3	651.0	1.00
2.9	17.4	8.9	97.9	-87.2	616.1	1.30
3.4	18.9	8.6	96.4	-86.9	580.9	1.40
3.9	19.9	8.4	94.9	-85.4	569.9	2.00

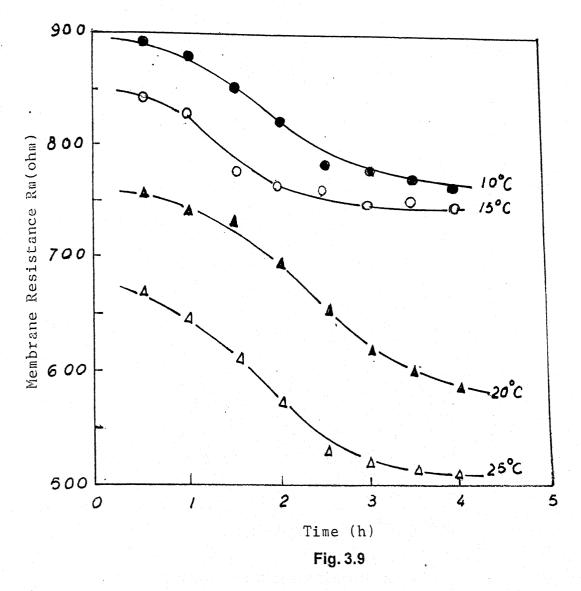
Table 3.12

Values of parameters for the diffusion of LiCl (0.1m/0.001m) through Polystyrene based cobalt phosphate membrane at $25\pm0.1^{\circ}\text{C}$

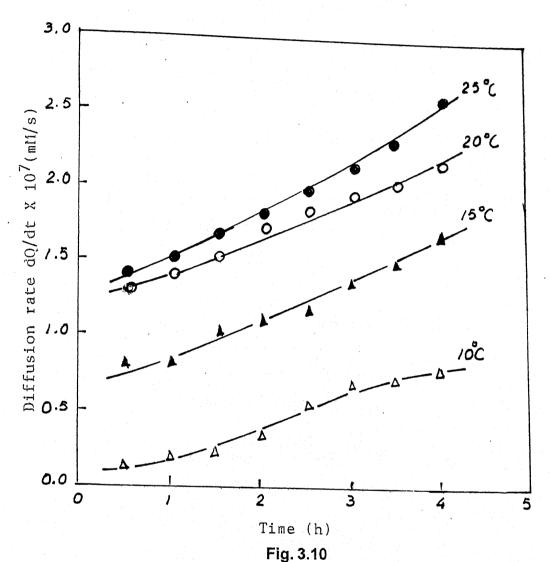
Time	Conc. (C ₁)	Eobs	Eŧ	Em	Rm	dQ/dt x107
(hr)	$(M) \times 10^4$	(mV)	(mV)	(mV)	(ohm)	(millimol/S)
0.4	13.4	7.6	109.9	-100.9	666.5	0.48
0.9	14.9	7.4	108.9	-99.2	646.9	0.54
1.4	16.4	7.0	107.9	-98.4	609.9	0.90
1.9	17.9	6.6	107.1	-97.0	569.9	1.20
2.4	18.4	5.9	105.9	-95.4	530.9	1.60
2.9	18.9	5.5	104.6	-94.0	519.9	2.10
3.4	19.4	5.4	103.1	-92.3	509.9	2.20
3.9	20.9	5.1	101.9	-91.5	509.9	2.40



Plots of membrane potential E_m (mV) against Time (h) at different temperatures across polystyrene based cobalt phosphate membrane using LiCl electrolyte.



Plots of membrane resistance R_m (ohm) against Time (h) at different temperatures across polystyrene based cobalt phosphate membrane using LiCl electrolyte.



Plots of diffusion rate dQ/dt (mM/s) against Time (h) at different temperatures polystyrene based across cobalt phosphate membrane using LiCl electrolyte.

Table 3.13

Values of parameters for the diffusion of CaCl₂ (0.1m/0.001m) through Polystyrene based cobalt phosphate membrane at 10±0.1°C

Time	Conc. (C1)	T	-			
(hr)	(M) x 10 ⁴	$\mathbf{E_{obs}}$ (mV)	E _ŧ (mV)	E _m	Rm	dQ/dt x107
0.4	10.9	17	•	(mV)	(ohm)	(millimol/8)
0.0		4.7	91.4	-88.6	615.2	0.37
0.9	12.9	4.4	90.4	-86.1	609.9	0.47
1.4	14.4	4.0	89.4	-84.3	581.7	0.58
1.9	16.4	3.7	88.4	-81.2	596.6	
2.4	17.9	3.3	87.4	-79.9		0.65
2.9	19.4			-19.9	565.4	0.78
		2.8	86.2	-78.7	564.3	0.80
3.4	21.9	2.4	84.9	-76.3	556.9	0.90
3.9	22.9	2.0	83.7	-76.2	549.9	0.90

Table 3.14

Values of parameters for the diffusion of CaCl2 (0.1 m/0.001 m) through Polystyrene based cobalt phosphate membrane at $15\pm0.1^{\circ}C$

Time	Conc. (C ₁)	Eobs	Eŧ	Em	Rm	dQ/dt x10 ⁷
(hr)	$(M) \times 10^4$	(mV)	(mV)	(mV)	(ohm)	(millimol/S)
0.4	11.9	0.0	101.4	-93.9	517.1	0.62
0.9	14.4	-0.4	99.4	-90.5	512.6	0.75
1.4	16.9	-0.8	97.6	-86.9	499.9	0.76
1.9	17.9	-1.4	96.4	-86.3	464.9	0.81
2.4	18.9	-1.7	95.4	-85.6	458.7	0.82
2.9	19.9	-2.1	94.4	-84.7	462.9	0.82
3.4	21.9	-2.6	93.6	-83.0	456.9	1.00
3.9	22.9	-2.9	92.4	-82.7	461.9	1.10

Table 3.15

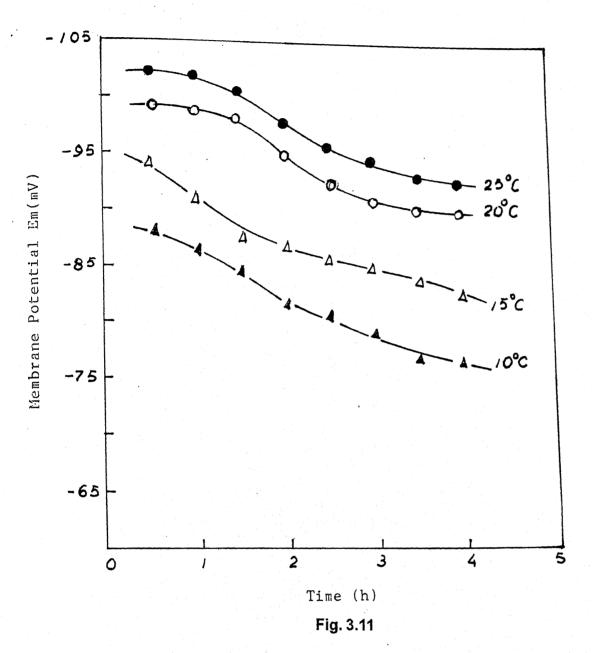
Values of parameters for the diffusion of CaCl2 (0.1m/0.001m) through Polystyrene based cobalt phosphate membrane at $20\pm0.1^{\circ}C$

Time	Conc. (C ₁)	Eobs	Eŧ	73		
(hr)	(M) x 10 ⁴	(mV)	(mV)	E _m (mV)	R _m (ohm)	dQ/dt x10 ⁷ (millimol/8)
0.4	11.9	-3.4	106.4	-99.1	•	
0.9	12.4	-3.9	105.2	-99.0	399.9 35.9	0.71 0.81
1.4	13.9	-4.4	103.7	-97.2	374.9	0.85
1.9	15.9	-4.8	102.4	-94.1	361.9	1.10
2.4	17.9	-5.2	101.1	-91.6	345.4	1.20
2.9	19.4	-5.7	99.4	-90.3	342.2	1.20
3.4	19.9	-5.9	98.4	-90.0	349.9	1.20
3.9	19.9	-6.1	98.4	-89.9	349.9	1.20

Table 3.16

Values of parameters for the diffusion of CaCl2 (0.1 m/0.001 m) through Polystyrene based cobalt phosphate membrane at $25\pm0.1^{\circ}C$

Time	Conc. (C1)	Eobs	Eŧ	E _m	Rm	dQ/dt x10 ⁷
(hr)	(hr) $(M) \times 10^4$	(mV)	(mV)	(mV)	(ohm)	(millimol/S)
0.4	11.9	-5.0	111.4	-102.4	284.7	1.3
0.9	12.9	-5.4	110.4	-101.6	274.9	1.5
1.4	13.9	-5.9	109.4	-100.3	272.0	1.5
1.9	15.9	-6.4	108.6	-97.3	259.9	1.9
2.4	17.4	-6.9	107.4	-95.4	253.9	2.2
2.9	18.9	-7.4	106.1	-94.1	245.0	2.6
3.4	19.9	-7.9	104.6	-93.3	240.9	3.0
3.9	20.9	-8.2	103.4	-92.6	239.9	3.1
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Plots of membrane potential E_m (mV) against Time (h) at different temperatures across polystyrene based cobalt phosphate membrane using $CaCl_2$ electrolyte

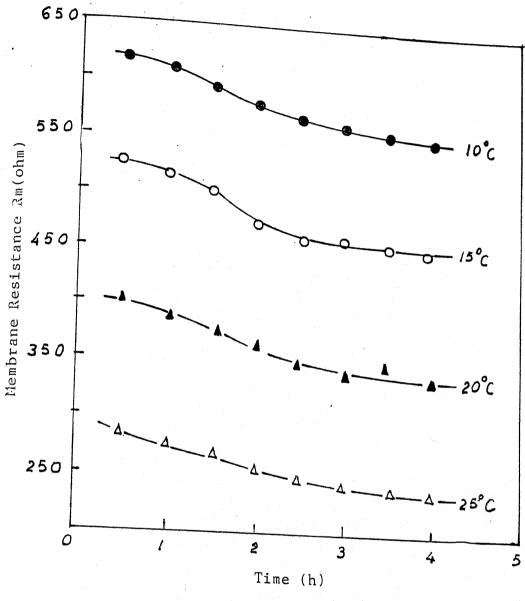
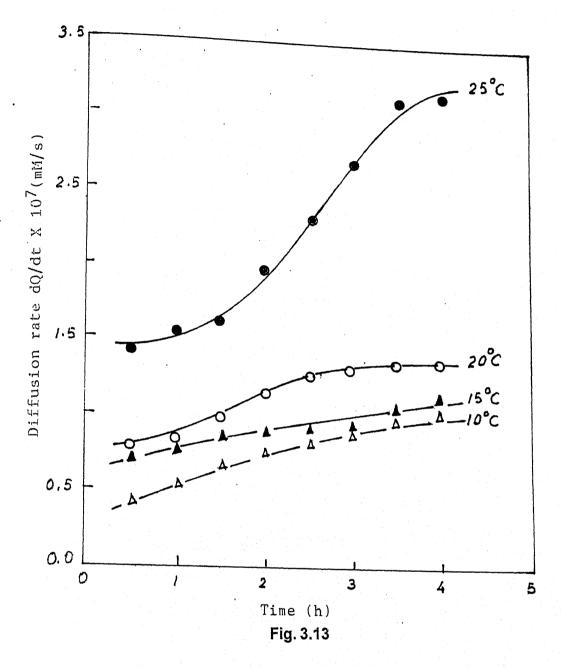


Fig. 3.12

Plots of membrane resistance $R_{\rm m}$ (ohm) against Time (h) at different temperatures across polystyrene based cobalt phosphate membrane using CaCl₂ electrolyte.



Plots of diffusion rate dQ/dt (mM/s) against Time (h) at different temperatures across polystyrene based cobalt phosphate membrane using CaCl₂ electrolyte.

Table 3.17

Values of parameters for the diffusion of BaCl2 (0.1m/0.001m) through Polystyrene based cobalt phosphate membrane at $10\pm0.1^{\circ}C$

Time	Conc. (C1)	Eobs	E _ŧ	Т		
(hr)	$(M) \times 10^4$	(mV)	(mV)	E _m (mV)	R _m (ohm)	dQ/dt x10 ⁷
0.4	10.4	1.4	94.4	-93.0	*	(millimol/S)
0.9	11.4	1.0	93.2		429.9	0.07
1.4	13.4	0.6		-91.2	424.9	0.09
1.9	14.4		92.4	-87.7	424.9	0.39
2.4	15.9	0.0	91.4	-87.2	431.9	0.40
2.9		-0.7	90.4	-86.2	423.3	0.41
	17.9	-1.4	89.2	-83.7	422.5	0.53
3.4	19.4	-1.7	87.9	-82.3	416.5	0.57
3.9	20.9	-1.9	86.7	-80.8	415.9	0.73

Table 3.18

Values of parameters for the diffusion of BaCl2 (0.1m/0.001m) through Polystyrene based cobalt phosphate membrane at $15\pm0.1^{\circ}C$

Time	Conc. (C ₁)) Eobs Et	Eŧ	E _m (mV)	R _m	dQ/dt x10 ⁷
(hr)	$(M) \times 10^4$	(mV)	(m V)		(ohm)	(millimol/S)
0.4	10.9	-2.6	102.9	-97.2	339.9	0.59
0.9	11.4	-2.9	101.9	-96.9	333.2	0.66
1.4	12.9	-3.6	100.1	-95.4	339.9	0.66
1.9	14.9	-3.9	98.9	-92.3	331.9	0.83
2.4	15.4	-4.6	97.9	-91.8	330.9	0.88
2.9	16.9	-5.1	96.9	-90.6	229.9	0.90
3.4	18.9	-5.7	95.1	-88.3	326.9	1.00
3.9	19.9	-5.9	93.9	-87.4	326.9	1.10

Table 3.19

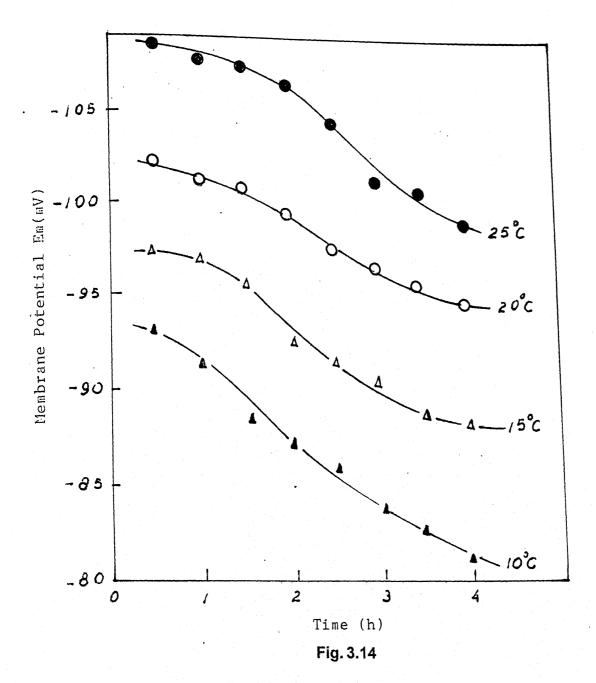
Values of parameters for the diffusion of BaCl₂ (0.1m/0.001m) through Polystyrene based cobalt phosphate membrane at 20±0.1°C

Time	Conc. (C1)	Eobs	Eŧ	Em	ъ	40/44-107
(hr)	(M) x 10 ⁴	(mV)	(mV)	(mV)	R _m (ohm)	dQ/dt x10 ⁷ (millimol/8)
0.4	10.9	-5.9	109.3	-102.2	290.5	1.0
0.9	11.9	-6.4	108.3	-100,9	287.5	1.0
1.4	12.4	-6.7	106.4	-100.6	289.9	1.1
1.9	13.4	-6.9	105.4	-99.1	288.9	1.2
2.4	14.9	-7.4	103.9	-97.3	287.9	1.3
2.9	15.9	-7.8	102.3	-96.0	287.9	1.3
3.4	17.4	-8.0	100.9	-95.2	286.9	1.5
3.9	17.9	-8.4	99.4	-94.2	204.9	1.7

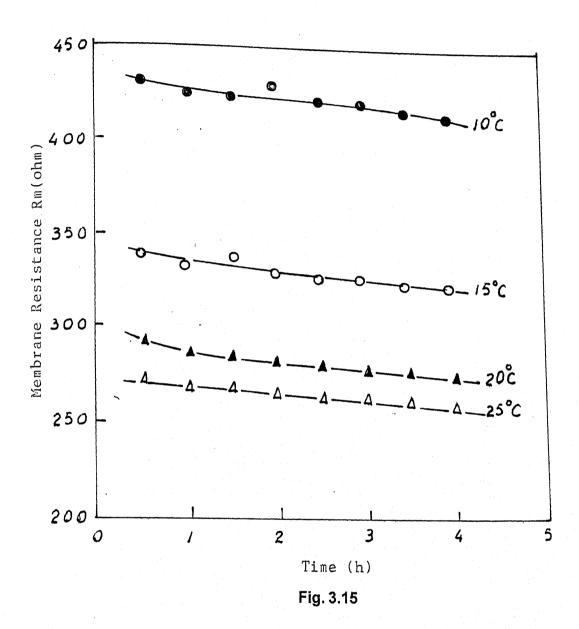
Table 3.20

Values of parameters for the diffusion of BaCl2 (0.1 m/0.001 m) through Polystyrene based cobalt phosphate membrane at $25\pm0.1^{\circ}C$

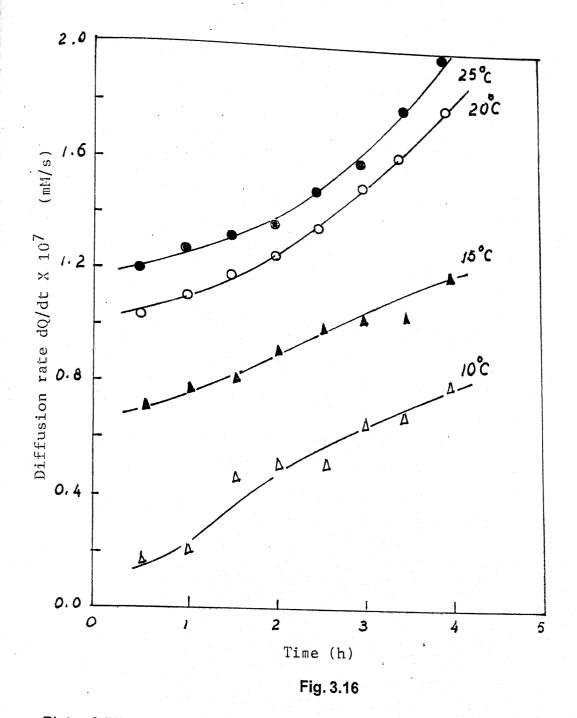
Time	Conc. (C ₁)	$\mathbf{E}_{\mathbf{obs}}$ $\mathbf{E}_{\dot{c}}$ (mV) (mV)	Em	Rm	dQ/dt x10 ⁷	
(hr)	$(M) \times 10^4$		(m V)	(m V)	(ohm)	(millimol/S)
0.4	10.4	-9.0	114.4	-108.7	274.9	1.1
0.9	10.9	-9.6	113.4	-107.5	766.9	1.2
1.4	11.4	-9.9	112.4	-106.9	274.9	1.2
1.9	12.4	-11.5	111.6	-106.2	265.5	1.3
2.4	13.9	-10.9	110.4	-104.1	266.9	1.4
2.9	15.9	-11.4	109.1	-101.1	268.9	1.5
3.4	16.9	-11.9	107.6	-100.4	264.6	1.7
3.9	18.9	-12.7	106.4	-98.3	260.6	1.8



Plots of membrane potential E_m (mV) against Time (h) at different temperatures across polystyrene based cobalt phosphate membrane using $BaCl_2$ electrolyte.



Plots of membrane resistance R_m (ohm) against Time (h) at different temperatures across polystyrene based cobalt phosphate membrane using $BaCl_2$ electrolyte.



Plots of diffusion rate dQ/dt (mM/s) against Time (h) at different temperatures across polystyrene based cobalt phosphate membrane using BaCl₂ electrolyte.

Table 3.21

Values of parameters for the diffusion of MgCl2 (0.1m/0.001m) through Polystyrene based cobalt phosphate membrane at $10\pm0.1^{\circ}C$

Conc. (C ₁)	Eobs	Eŧ	Em	Rm	dQ/dt x10 ⁷
$(M) \times 10^4$	(mV)	(m V)	(mV)	(ohm)	(millimol/S)
11.4	10.35	55.0	-59.4	459.9	0.48
12.9	10.00	53.5	-57.0	429.9	0.64
14.9	9.65	51.9	-53.9	427.9	0.77
16.4	9.10	50.7	-52.2	349.9	0.89
17.4	8.60	49.3	-48.9	275.9	1.30
19.4	8.25	47.8	-48.2	270.9	1.40
20.4	8.00	46.3	-47.7	270.9	1.40
21.4	7.90	44.9	-47.3		1.50
	(M) x 10 ⁴ 11.4 12.9 14.9 16.4 17.4 19.4 20.4	(M) x 104 (mV) 11.4 10.35 12.9 10.00 14.9 9.65 16.4 9.10 17.4 8.60 19.4 8.25 20.4 8.00	(M) x 10 ⁴ (mV) (mV) 11.4 10.35 55.0 12.9 10.00 53.5 14.9 9.65 51.9 16.4 9.10 50.7 17.4 8.60 49.3 19.4 8.25 47.8 20.4 8.00 46.3	(M) x 10 ⁴ (mV) (mV) (mV) 11.4 10.35 55.0 -59.4 12.9 10.00 53.5 -57.0 14.9 9.65 51.9 -53.9 16.4 9.10 50.7 -52.2 17.4 8.60 49.3 -48.9 19.4 8.25 47.8 -48.2 20.4 8.00 46.3 -47.7	(M) x 10 ⁴ (mV) (mV) (mV) (mV) (ohm) 11.4 10.35 55.0 -59.4 459.9 12.9 10.00 53.5 -57.0 429.9 14.9 9.65 51.9 -53.9 427.9 16.4 9.10 50.7 -52.2 349.9 17.4 8.60 49.3 -48.9 275.9 19.4 8.25 47.8 -48.2 270.9 20.4 8.00 46.3 -47.7 270.9

Table 3.22

Values of parameters for the diffusion of MgCl2 (0.1m/0.001m) through Polystyrene based cobalt phosphate membrane at $15\pm0.1^{\circ}$ C

Time	Conc. (C ₁)	Eobs	E _t	Em	Rm	dQ/dt x107
(hr)	$(M) \times 10^4$	(mV)	(mV)	(mV)	(ohm)	(millimol/S)
0.4	10.9	7.45	60.0	-62.3	367.1	0.86
0.9	12.4	7.05	58.5	-61.7	349.9	0.90
1.4	13.4	6.40	56.9	-59.7	346.6	1.20
1.9	16.4	5.90	55.7	-56.6	336.6	1.30
2.4	17.9	5.40	54.3	-54.7	310.2	1.50
2.9	18.9	4.60	52.8	-51.9	257.9	1.70
3.4	18.9	4.00	51.3	-51.2	254.4	1.70
3.9	19.9	3.90	49.9	-51.2	239.4	1.80

Table 3.23

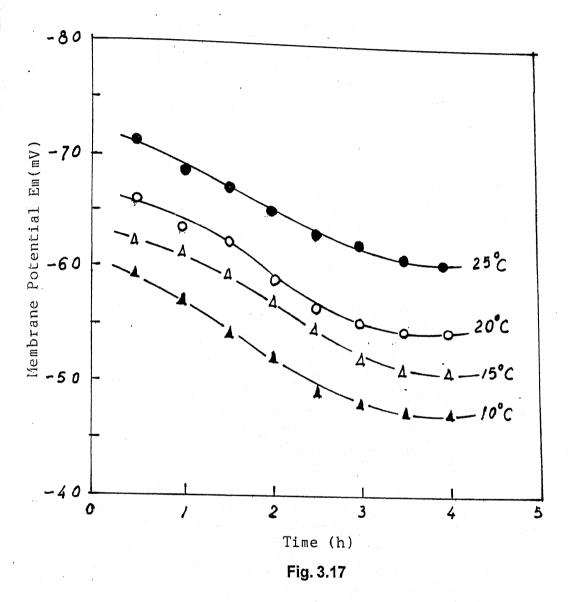
Values of parameters for the diffusion of MgCl₂ (0.1m/0.001m) through Polystyrene based cobalt phosphate membrane at 20±0.1°C

Time	Conc. (C1)	Eobs Et	Em	Rm	dQ/dt x10 ⁷	
(hr)	$(M) \times 10^4$	(mV)	(mV)	(mV)	(ohm)	(millimol/S)
0.4	12.4	5.65	64.2	-65.9	310.7	1.2
0.9	13.9	5.40	62.7	-63.4	299.9	1.4
1.4	15.4	5.10	61.2	-62.0	289.9	1.4
1.9	16.9	4.90	59.7	-58.1	277.6	1.5
2.4	18.9	4.40	58.3	-56.3	211.1	1.6
2.9	19.9	4.00	56.8	-55.5	199.9	2.1
3.4	20.9	3.70	55.3	-54.6	169.9	2.1
3.9	20.9	3.60	53.9	-54.5	169.9	2.4

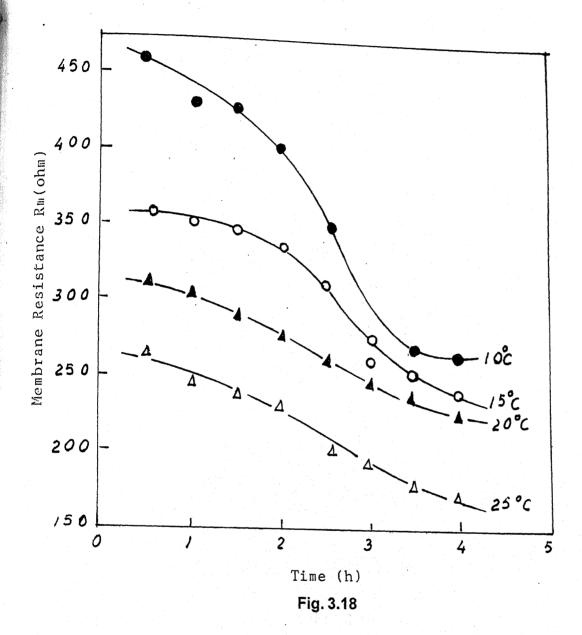
Table 3.24

Values of parameters for the diffusion of MgCl2 (0.1m/0.001m) through Polystyrene based cobalt phosphate membrane at $25\pm0.1^{\circ}$ C

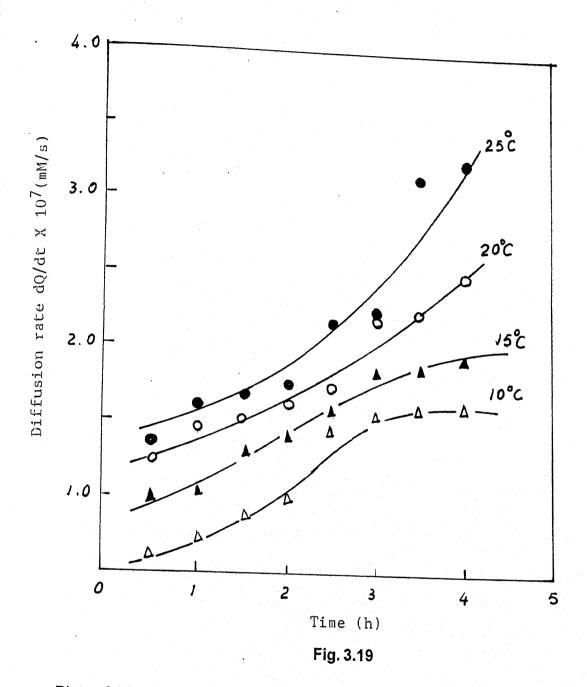
Time	Conc. (C1)	E obs Et	Em	Rm	dQ/dt x107	
(hr)	(M) x 10 ⁴	(mV)	(mV)	(mV)	(ohm)	(millimol/S)
0.4	10.9	2.90	68.2	-71.2	266.5	1.3
0.9	12.4	2.65	66.7	-68.5	244.3	1.5
1.4	13.4	2.35	65.2	-67.0	239.9	1.6
1.9	14.9	2.00	63.7	-65.1	238.3	1.7
2.4	16.4	1.70	62.3	-63.0	199.9	2.1
2.9	17.4	1.20	60.8	-62.3	189.9	2.2
3.4	17.9	0.90	58.3	-61.0	180.1	3.1
3.9	18.9	0.40	57.9	-61.3	152.9	3.2



Plots of membrane potential E_m (mV) against Time (h) at different temperatures across polystyrene based cobalt phosphate membrane using ${\rm MgCl_2}$ electrolyte.



Plots of membrane resistance R_m (ohm) against Time (h) at different temperatures across polystyrene based cobalt phosphate membrane using $MgCl_2$ electrolyte.



Plots of diffusion rate dQ/dt (mM/s) against Time (h) at different temperatures across polystyrene based cobalt phosphate membrane using MgCl₂ electrolyte.

Table 3.25

Values of parameters for the diffusion of AlCl3 (0.1m/0.001m) through Polystyrene based cobalt phosphate membrane at 10±0.1°C

Time	Conc. (C1)	Eobs	Et	Em	Rm	dQ/dt x10 ⁷
(hr)	$(M) \times 10^4$	(mV)	(mV)	(mV)	(ohm)	(millimol/S)
0.4	10.4	18.1	84.9	-99.9	499.9	0.5
0.9	11.4	19.5	83.7	-99.6	499.9	0.9
1.4	13.4	21.7	82.3	-97.9	494.9	1.1
1.9	14.4	21.4	81.3	-95.9	489.9	1.4
2.4	15.9	22.2	80.9	-94.4	487.9	1.9
2.9	17.9	21.9	79.6	-91.9	479.9	2.2
3.4	19.4	215	76.9	-90.9	476.1	2.6
3.9	20.9	22.3	75.9	-88.9	469.9	2.7

Table 3.26

Values of parameters for the diffusion of AlCl3(0.1m/0.001m) through Polystyrene based cobalt phosphate membrane at $15\pm0.1^{\circ}$ C

Time	Time Conc. (C ₁) (hr) (M) \times 10 ⁴	\mathbf{E}_{obs} \mathbf{E}_{c}	Em	R _m	dQ/dt x10 ⁷	
(hr)		(mV)	(mV)	(mV)	(ohm)	(millimol/S)
0.4	10.9	-19.1	88.9	-102.4	459.9	1.2
0.9	11.4	19.4	87.9	-100.9	458.9	1.8
1.4	12.9	-21.2	86.9	-99.9	457.9	2.0
1.9	14.9	-22.2	85.9	-97.4	450.9	2.4
2.4	15.4	-20.2	84.9	94.9	449.9	2.4
2.9	16.9	19.5	83.7	92.4	440.4	3.1
3.4	18.9	-19.9	82.4	90.9	435.3	3.0
3.9	19.9	-20.9	81.2	-89.9	431.9	4.8

Table 3.27

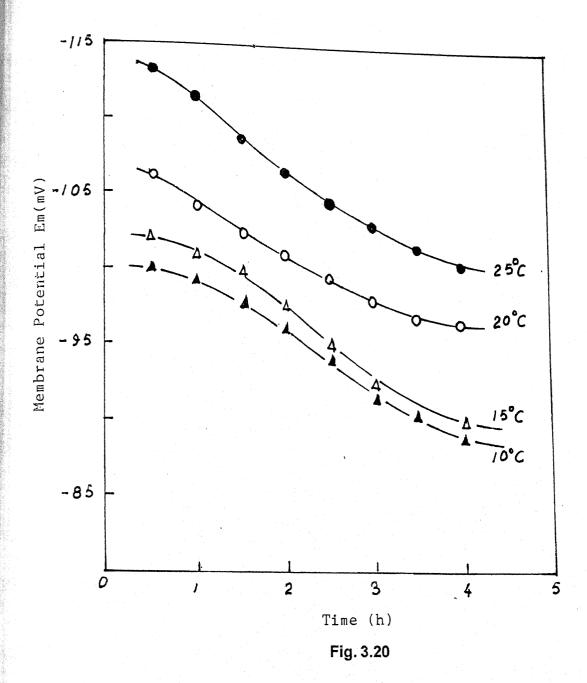
Values of parameters for the diffusion of AlCl3 (0.1m/0.001m) through Polystyrene based cobalt phosphate membrane at $20\pm0.1^{\circ}\text{C}$

Time	Conc. (C1)	Eobs	Et	Em	Rm	dQ/dt x10 ⁷
(hr)	$(M) \times 10^4$	(mV)	(mV)	(mV)	(ohm)	(millimol/S)
0.4	10.9	-21.3	96.9	-106.0	439.9	3.9
0.9	11.9	-22.1	95.4	-103.9	435.7	4.3
1.4	12.4	21.5	94.1	-102.1	434.4	4.7
1.9	13.4	-22.0	92.8	-100.9	431.4	5.2
2.4	14.9	-22.9	91.2	-99.4	412.1	5.4
2.9	15.9	-22.9	89.9	-97.9	408.9	5.9
3.4	17.4	-23.8	88.9	-96.9	405.1	6.4
3.9	17.9	-23.9	87.9	-96.4	389.9	6.7

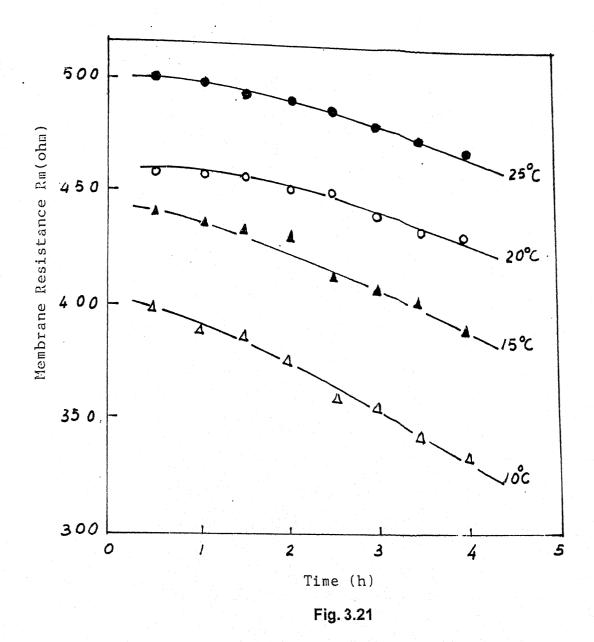
Table 3.28

Values of parameters for the diffusion of AlCl₃ (0.1m/0.001m) through Polystyrene based cobalt phosphate membrane at 25±0.1°C

Time	Conc. (C1)	Eobs	Eŧ	Em	Rm	dQ/dt x107
(hr)	$(M) \times 10^4$	(mV)	(mV)	(mV)	(ohm)	(millimol/S)
0.4	10.4	-27.0	100.4	-113.1	399.9	5.3
0.9	10.9	-27.4	99.1	-111.4	391.6	5.4
1.4	11.4	-25.4	97.9	-108.4	389.9	5.7
1.9	12.4	-23.3	96.7	-105.9	377.3	6.5
2.4	13.9	-25.9	95.2	-104.4	359.9	6.4
2.9	15.9	-27.2	94.1	-102.9	357.9	7.5
3.4	16.9	-30.5	92.9	-101.4	341.9	8.9
3.9	18.9	-30.7	91.9	-99.9	299.9	9.4



Plots of membrane potential E_m (mV) against Time (h) at different temperatures across polystyrene based cobalt phosphate membrane using AlCl₃ electrolyte.



Plots of membrane resistance R_m (ohm) against Time (h) at different temperatures across polystyrene based cobalt phosphate membrane using AlCl₃ electrolyte.

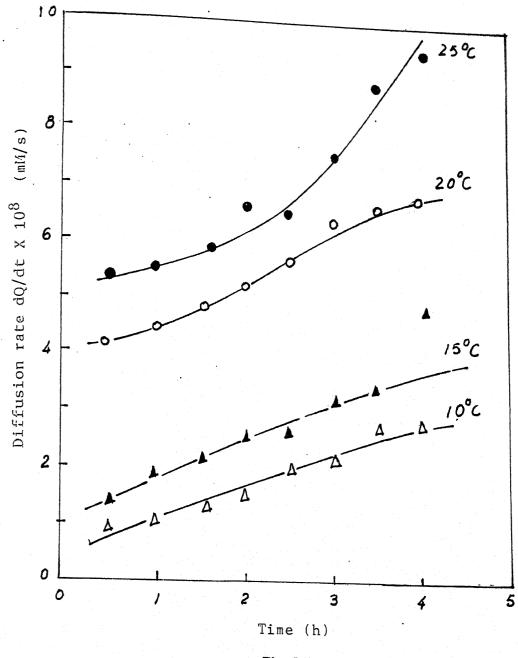


Fig. 3.22

Plots of diffusion rate dQ/dt (mM/s) against Time (h) at different temperatures across polystyrene based cobalt phosphate membrane using AlCl₃ electrolyte.

Table 3.29

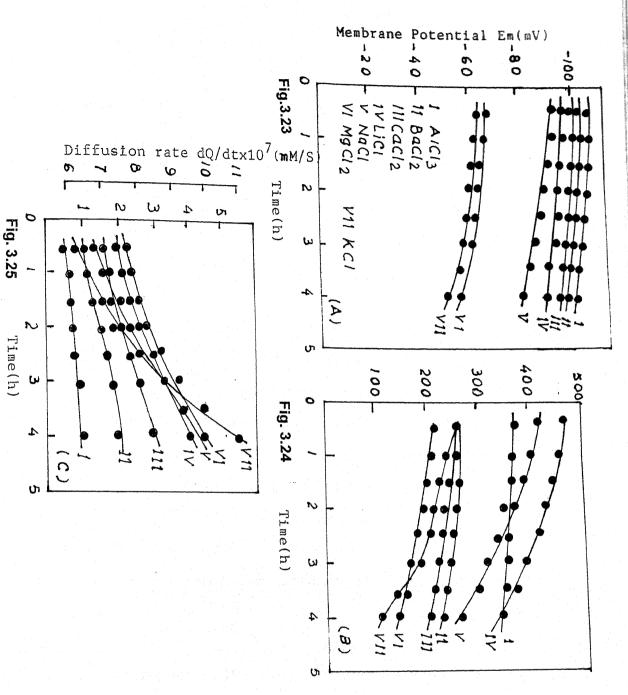
hour periods through Polystyrene based cobalt phosphate membrane at 25 \pm 1°C Values of parameters for the diffusion of monovalent, divalent and trivalent electrolytes at the end of 1/2 and 4

AlCl3	MgCl2	BaCl2	CaCl2	LiC1	NaCl	KCl		Electrolyte	Parameter
-27.1	3.0	-9.1	5.1	7.7	11.7	40.1	1/2 h		Eobs
-30.8	0.5	-12.8	-8.3	5.2	9.8	38.5	$\frac{1}{2}h \leftrightarrow 4h$		Eobs (mV)
100.5	68.3	114.5	111.5	110.0	101.5	99.5	1/2 h		Ť.
92.0	58.0	106.5	103.5	102.0	93.0	91.0	$\frac{1}{2}h \leftrightarrow 4h$		Et (mV)
-113.2	-71.3	-108.8	-102.5	-101.4	-98.5	-68.6	1/2 h		Em
-100.0	-61.4	-98.4	-92.7	-91.6	-84.0	-55.9	$\frac{1}{2}h \leftrightarrow 4h$		Em (mV)
400.0	266.6	275.0	284.8	666.6	540.0	283.4	1/2 h		Rm (ohm)
300.0	153.0	260.7	240.0	500.0	370.0	215.0	$\frac{1}{2}h \leftrightarrow 4h$		ohm)
0.5	1.4	1.2	1	0.6	.	4.3	1/2 h	(milli	dQ/d
0.9	3.3	1.9	3.2	2.5	2.7	6,8	$\frac{1}{2}h \leftrightarrow 4h$	(milli mol/s)	dQ/dtx10 ⁷

Table 3.30

hour periods through Polystyrene based nickel phosphate membrane at 25 \pm $1^{\rm o}{\rm C}$ Values of parameters for the diffusion of monovalent, divalent and trivalent electrolytes at the end of 1/2 and 4

Parameter	Eobs (mV)	(mV)	닭 (Et (mV)	Em (mV)	mV)	R _m (ohm)	ohm)	dQ/dtx10 ⁷	tx10 ⁷
Electrolyte									(milli mol/s)	nol/s)
	$\frac{1}{2}h \leftrightarrow 4h$	$\rightarrow 4h$	$\frac{1}{2}h \leftrightarrow 4h$	↔4 <i>h</i>	$\frac{1}{2}h\leftrightarrow 4h$	$\leftrightarrow 4h$	$\frac{1}{2}h \leftrightarrow 4h$	→4 <i>h</i>	$\frac{1}{2}h \leftrightarrow 4h$	$\rightarrow 4h$
KCI	44.1	42.0	98.0	91.0	-64.4	-51.4	261.5	110.0	6.4	
NaCl	15.7	13.0	99.5	97.0	-94.5	-80.2	426.0	285.2	1.3	A
LiC1	10.5	8.3	108.0	100.0	-98.0	-88.0	475.5	342.2	2.1	4.0
CaCl2	-4.0	-7.0	110.0	103.0	-101.3	-91.4	265.0	205.0	1.6	2.9
BaCl ₂	-6.5	-8.3	111.5	103.5	-106.2	-94.4	260.0	235.0	1.0	1.9
MgCl2	5.7	3.5	66.2	55.0	-68.0	-58.4	218.0	140.0	2.1	4.0
AICl3	-24.1	-25.0	99.0	90.5	-110.2	-97.0	382.2	340.8	0.6	0.8



Membrane Resistance Rm(ohm)

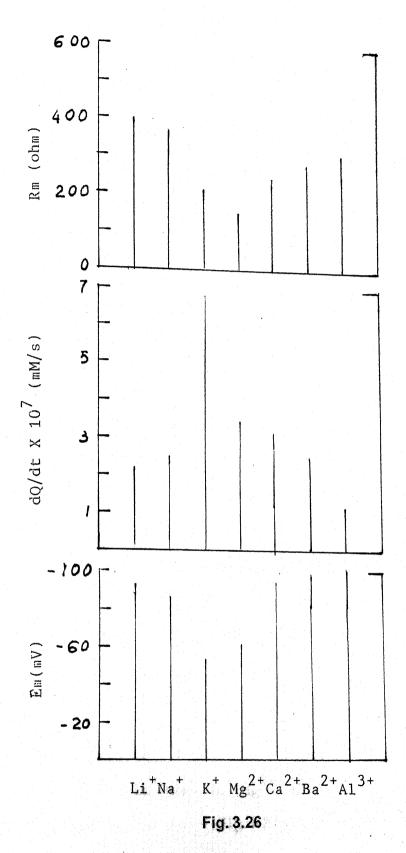
$$\frac{dQ}{dt} = \frac{1}{4FR_m} \left[\left(\frac{E_c^{\dagger}}{3} - E_m \right) \right] \left[\left(\frac{E_m}{E_c^{\dagger}} + 1 \right) \right]$$
(3.6)

The values of membrane potential E_m , membrane resistance R_m , and the diffusion rate dQ/dt derived from the experimental data and using eqs. (3.4-3.6) for both cobalt and nickel phosphate membranes in contact with different concentrations of various electrolytes are given in Tables 3.1 - 3.30, and also depicted in Figs. 3.2 - 3.25 against the diffusion time while comparative values for various cations are shown in Figs. 3.26 and 3.27.

Tables 3.1 – 3.30 show that the membrane resistance R_m sequence for both the membranes at any given time for the alkali metal ions is Li⁺ > Na⁺ > K⁺; for alkaline earth metal ions is Ba²⁺ > Ca²⁺ > Mg ²⁺ and for aluminium it is highest. This sequence refers to the fact that there are very few coions in the membrane phase, and so in both the cases, the current carrying species are the cations. The charge on the ion has a very big effect on the mobility of the ions in the membranes. As the charge on the counterions is increased, the membrane resistance increases. This may be ascribed to be due to the increase in the ion association with the membrane exchange groups. This is in agreement with the findings of Lakshminarayanaiah et al. (19), Kotani (35) and Gregor and co-workers (36) for the AMF C-103 membrane and our own findings with polystyrene based inorganic precipitate membranes (22,33, 24).

The values of Em decreases with time though almost to a negligible extent, as can be seen in Fig. 3.23 for various diffusing electrolytes through polystyrene based nickel phosphate membrane. The slight

proposition and transmission of the con-



Plots of E_m, R_m, and dQ/dt against various electrolytes across polystyrene based cobalt phosphate membrane at 25°C.

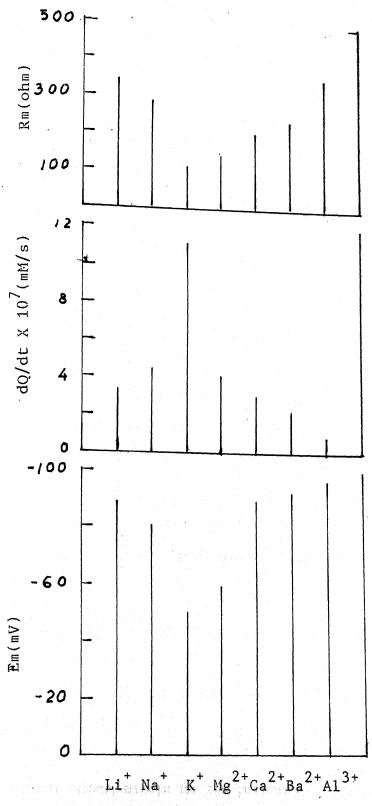


Fig. 3.27

Plots of E_m, R_m, and dQ/dt against various electrolytes across polystyrene based nickel pohsphate membrane at 25°C.

change in E_m may be due to the small changes produced in the concentration of electrolyte solutions during the diffusion processes. The membrane potential sequence for alkali metal ions was $Li^+>Na^+>K^+$ and for multivalent cations it was $Al^{3+}>Ba^{2+}>Ca^{2+}>Mg^{2+}$. This sequence of membrane potential point towards the fact that multivalent ions are more strongly adsorbed on the membrane skeleton than univalent ions and that aluminium being most strongly adsorbed (19).

The values of diffusion rate dQ/dt for various cations were calculated from the predetermined values of membrane potential Em and membrane resistance Rm using eqs. (3.4 - 3.6). The diffusion of electrolytes through the membrane is slower than in free solution. This may be due to various reasons: (a) only a part of framework is available for free diffusion, (b) the diffusion paths in the membrane phase are more tortuous and therefore longer, (c) the large hydrated ions in the narrow mesh region of the membrane be impeded in their mobility by the framework and (d) the interaction of the diffusing species with the fixed groups on the membrane matrix. The diffusion rate sequence of cations diffusing through was $K^+ > Na^+ > Li^+$ and the membrane $Mg^{2+} > Ca^{2+} > Ba^{2+} > Al^{3+}$. This diffusion rate sequence on the basis of Eisenman-Sherry model of membrane selectivity (37, 38) point towards weak field strength of charge groups attached to the membrane matrix. This is in agreement with our earlier findings of inorganic precipitate membranes (22, 23, 24).

Parchment paper, except for the presence of some stray and end carboxyl groups, contains very few fixed groups. Deposition of inorganic precipitate gives rise to a net negative charge on the membrane surface in the case of dilute solutions of electrolyte (1:1) leading to the type of ionic distribution associated with the electrical double layer. However, use of concentrated electrolyte (1:1) or (2:1) or (3:1) leaves a net positive charge on the membrane surface due to the preferential adsorption of cations. This type of charge reversal is not peculiar to these systems. Rosenberg et al. (39) found in the case of Thorium counterions, negative electroosmotic transport of water. The ion was so strongly adsorbed on a cation exchange membrane that it conferred anion selectivity to the membrane and thus water was transferred in the opposite direction. Similarly schulz (40) found, in the case of sodium diphosphate, adsorption of the diphosphate anion on the surface of the anion exchange membrane, permplex A-100. This reversed the charge on the membrane and also the direction of water flow.

The system under consideration may be taken as having charged capillary structures or gels which can be judged in the light of classical fixed charge theory of Teorell (41); Meyer and Sievers (42); Sollner (43); Gregor (44), Schimid (45-46), owen (47) and stokes (48). Flow of electrolyte by diffusion because of the presence of a net charge (-Ve or +Ve) on the membrane gives rise to the membrane potential as opposed to the liquid junction potential ordinarily observed under similar conditions in the absence of the membrane, which regulates the flow of electrolyte by increasing the speed of slow moving ion and by decreasing the speed of the faster moving ion. The regulated rate of flow for various electrolytes through the investigated membranes follow the sequence $K^+ > Na^+ > Li^+$ and $Mg^{2+} > Ca^{2+} > Ba^{2+} > Al^{3+}$.

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Membrane porosity in relation to the size of the species (hydrated) flowing through the membrane seems to determine the above sequence. Although the sizes of the hydrated electrolytes are not known with certainty, there are a few tabulations (47, 48) of the number of moles of water associated with some electrolytes. However, in Fig. 3.28 a plot of permeability of different electrolytes (chlorides) against free energy of hydration of cations (49, 50) is given for both the membranes. It is seen that permeability decreases with increasing hydration energy, that is, greater size due to increase in hydration. This points to the fact that the electrolyte is diffusing along the pores or channels of dimensions adequate enough to allow the substance to penetrate the membrane. The state of hydration of the penetrating electrolyte may be considered to exist in a dynamic condition so that at higher temperatures considerably higher fraction F of the total number of a given kind would possess excess energy ΔE according to the Boltzmann distribution $f = e^{-\Delta E/RT}$ (R is the gas constant). Under these circumstances, those ionic species which have lost sufficient water of hydration to be smaller than the size of the pore would enter the membrane. In this way the permeability would increase with increase in temperature, subject, however, to the proviso that the membrane has undergone no irreversible change in its structure. That no such structural change is involved is evident from the linear plots of log dQ/ dt versus (1/T) given in Figs. 3.29 and 3.30. The slope of these lines which is equal to (Ea/ 2.303R) gave the activation energy Ea required for the diffusion process. The values so derived are given in Tables 3.31 and 3.32.

The diffusion rate dQ/dt (millimol/h) is related to diffusion coefficient \overline{D} (cm/sec) by the relation

F1 (4.25)

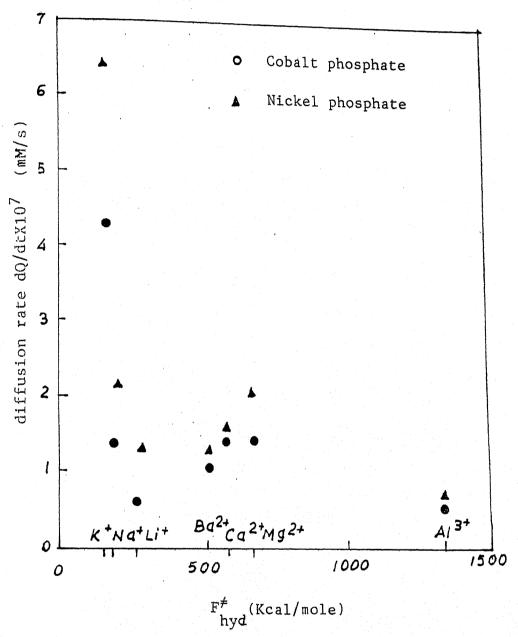


Fig. 3.28

Diffusion rate dQ/dt X 10^7 (mM/s) at 25° C for various electrolytes (Chloride) through both the polystyrene based membrane plotted against free energy ΔF^* of hydration of cations.

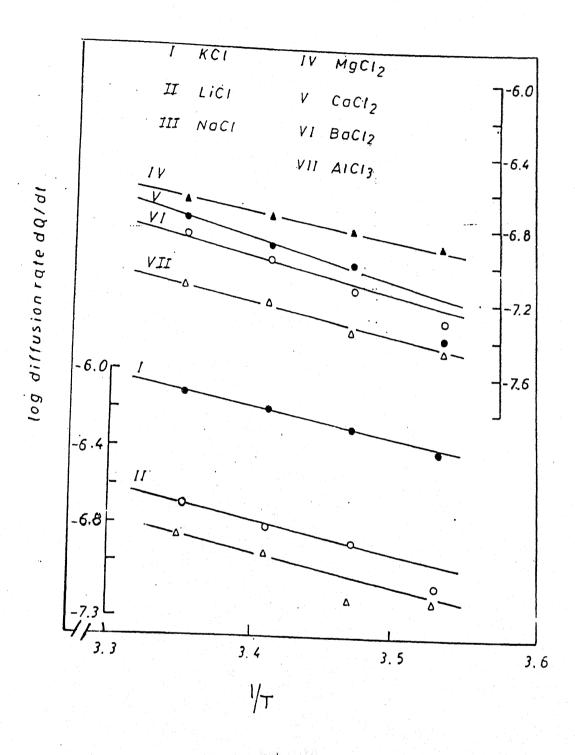


Fig. 3.29

Plots of dQ/dt against 1/T for various electrolytes across polystyrene based cobalt phosphate membrane at 25°C.

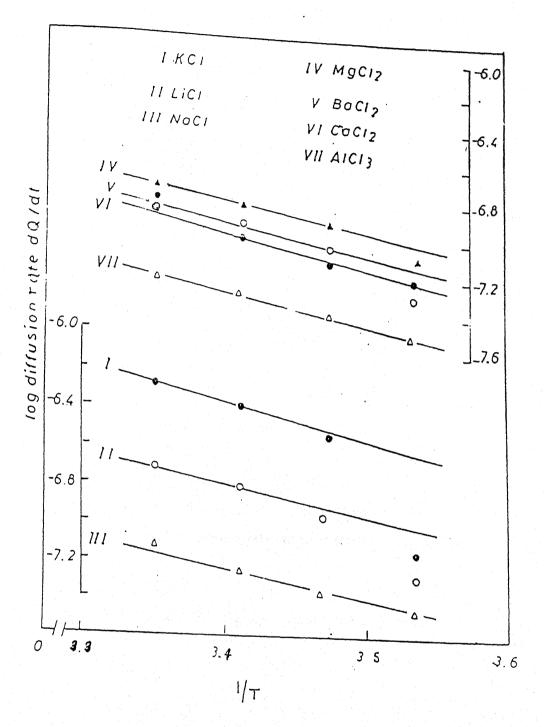


Fig. 3.30

Plots of log dQ/dt against 1/T for various electrolytes with polystyrene based nickel phosphate membrane at 25°C.

Table 3.31

Experimental activation energy E_a and other Thermodynamic parameters calculated from transition state theory of rate processes for polystyrene based cobalt phosphate membrane at $25\pm0.1^{\circ}C$

Parameter	Ea	Δ H ≠	ΔF	∆S *		
Electrolyte	(Kcal Mol ⁻¹)	(Kcal Mol-1)	(Kcal Mol-1)	(Kcal Mol-1)		
KCl	7.4	6.8	11.0	-14.0		
NaCl	6.7	6.1	11.3	-17.5		
LiCl	6.4	5.8	11.8	-20.2		
CaCl ₂	5.9	5.4	11.7	-21.4		
BaCl ₂	6.1	5.5	11.9	-21.5		
MgCl ₂	5.1	4.5	11.7	-24.5		
AlCl3	4.9	4.3	12.4	-27.2		

Table 3.32

Experimental activation energy E_a and other Thermodynamic parameters calculated from transition state theory of rate processes for polystyrene based nickel phosphate membrane at $25\pm0.1^{\circ}C$

Parameter	Ea	$\Delta \mathbf{H}^{\star}$	$\Delta \mathbf{F}^{\neq}$	ΔS [≠] (e.u.)	
Electrolyte	(Kcal Mol ⁻¹)	(Kcal Mol ⁻¹)	(Kcal Mol ⁻¹)		
KC1	7.1	6.5	10.8	-14.3	
NaCl	6.7	6.1	11.8	-19.2	
LiCl	6.2	5.6	11.6	-20.0	
CaCl ₂	5.9	5.3	11.7	-21.6	
BaCl ₂	5.6	5.0	11.9	-23.4	
MgCl2	5.5	4,9	11.6	-22.4	
AlCl3	4.6	4.0	12.3	-27.8	

$$\overline{D} = dQ/dt \times 10^{-6} / 3.6 \text{ A} \Delta C$$

(3.7)

Where A is the membrane area (24.6 cm²) and ΔC is the difference in the electrolyte concentration existing across the membrane. Since area of membrane and concentration difference of the electrolytes are constant, therefore \overline{D} is proportional to dQ/dt and thus the slopes of linear plots of log \overline{D} vs. (1/T) and of log dQ/dt vs. (1/T) will be equal.

The theory of absolute reaction rate (31) has been applied to diffusion processes in membrane by several investigators (31-33). According to Zwolinsky et al. (51), we have

$$\overline{D} = \lambda^2 (KT/dh) \exp{-\Delta F^{\neq}/RT}$$
 (3.8)

where K is Boltzmann constant, d is membrane thickness, h is Plank constant, and λ is average distance between equilibrium positions in the process of diffusion. ΔF^{\sharp} is the free energy of activation for diffusion and is related to enthalpy ΔH^{\sharp} and entropy ΔS^{\sharp} of activation of diffusion by Gibbs-Helmholtz equation.

$$\Delta \mathbf{F}^{\neq} = \Delta \mathbf{H}^{\neq} - \mathbf{T} \Delta \mathbf{S}^{\neq} \tag{3.9}$$

ΔH[≠] is related to Arrhenius energy of activation E_a by the equation

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$$\Delta H^{\neq} = E_a + RT \tag{3.10}$$

As the values of d and of the universal constants are known, values of ΔH^{\neq} , ΔS^{\neq} and ΔF^{\neq} can be calculated provided the value of λ is known.

Different investigators (31-33) have used values ranging from 1-5 A° for λ . In this work, a value of 1A° has been used in the calculations, and the values so derived for the different thermodynamic parameters are given in Tables 3.31 and 3.32. For purpose of comparison, in Table 3.33 are given the values of ΔS^* determined by various investigators for a variety of systems. The values of ΔS^* (see Table 3.33) are either positive or negative for membranes. There are a few values which are close to zero and correspond to liquid systems. According to Eyring and co-workers (51, 52), the values of ΔS^* indicate the mechanism of flow., large positive ΔS^* is interpreted to reflect breakage of bonds, while low values indicate that permeation has taken place without breaking bonds. The negative ΔS^* values are considered to indicate either formation of covalent bond between the permeating species and the membrane material or that the permeation through the membrane may not be the rate determining step.

On the contrary, Barrer (50,53,54) has developed the concept of "Zone activation" and applied it to the permeation of gases through polymer membranes. According to this zone hypothesis, a high ΔS^* , which has been correlated with high energy of activation for diffusion, means either the existence of a large zone of activation or the reversible loosening of more chain segments of the membrane. A low ΔS^* , Then means either a small zone of activation or no loosening of the membrane structure on permeation. In view of these differences in the interpretation of ΔS^* , Shuller et al. (55), who found negative ΔS^* values for sugar permeation through collodion membranes, have stated that "it would probably be correct to interpret the small negative values of ΔS^* mechanically as interstitial permeation of the membrane (minimum chain loosening) with partial immobilization in the membrane (small zone of

Table 3.33

Thermodynamic parameters ΔS^* for permeation of various substances through different systems

Diffusion system		Entropy			
Diffusing species	Medium	factor $\lambda [~e^{\Delta_{\mathbb{S}^{\#}}/}R]^{1/2},$	Δ S [*] , e.u.	Reference	
		A°			
Water	Water	11.0	9.5 >	1	
Phenol	Methyl alcohol	1.4	1.3		
Phenol	Benzene	1.4	1.3	31 ^b	
C2H2Br4	C2H2C4	1.0	0		
Bromine	CS ₂	0.4	-3.6		
Mannitole	Water	2.8	4.1	50b ^b	
H ₂	Butadiene-acrylonitrile	182	16.0		
	membrane				
N_2	Butadiene-acrylonitrile	130	14.7		
	membrane				
N ₂	Butadiene-methyl, Meth-	150	15.3		
	acrylate				
	Membrane			31 ^b 52 ^c	
Ar	Butadiene-methyle meth-	93	13.4		
	acrylate				
	Membrane				
N_2	Butadiene-polystyrene	24	7.8		
	membrane				

Contd

Ar	Butadiene-polystyrene	33	9.3	
	membrane		9.0	
H2	Neoprene membrane	74	12.4	
N_2	Neoprene membrane	215	16.7	31 ^b 52 ^c
Ar	Neoprene membrane	185	16.2	
H2	Chloroprene membrane	150	15.3	
H2	Silicone rubber membrane	1.3	-3.4	
•	(Sheet)			
N ₂	Silicone rubber membrane	0.85	-5.0	
	(Sheet)			
O2	Silicone rubber membrane	0.61	-6.3	ta e a composition
	(Sheet)			53
Не	Silicone rubber membrane	0.87	-4.9	
	(Sheet)			
Ar	Silicone rubber membrane	0.83	-5.1	
	(Sheet)			
H2	Glass membrane	4×10^{-2}	-17.1)
Не	Glass membrane	4 x 10 ⁻²	-17.1	
Sucrose	Collodion membrane	1.1 x 10 ⁻²	-22.2	
Lactose	Collodion membrane	4.3×10^{-2}	-16.8	
Mannitol	Collodion membrane	8.1 x 10 ⁻³	-23.4	32
Raffinose	Collodion membrane	2.4 x 10-2	-19.1	
H ₂ O (Sucrose	Collodion membrane	1.2×10^{-2}	-21.8	
Solution))
H ₂ O	n-Hexadecane liquid	2.8	-0.2	
H ₂ O	Hexamethyltetracoson	4.8	1.9	55
	liquid			

Contd

H ₂ O	Polyethylene membrane	20-103	
H ₂ O	Polyethylene membrane	3.9×10^3 25×10^3	28.4
H ₂ O	Liquid bilayer membrane	25 X 10°	35.8 56
	(Oxidized cholesterol)	5.5×10^{-2}	-15.8 > 51
H ₂ O (Endo- osmosis)	Arbacia eggs (unfertilized)	14.4 x 10 ³	3.16
Propionamide	Arbacia eggs (unfertilized)	26.9×10^3	34
Butyramide	Arbacia eggs (unfertilized)	12.1×10^4	34 40 30 ^d
Nonelectrolyte			
(glycerol,	Oxerythrocyte membrane	77	2.7
glycols			$\begin{array}{c c} 3.7 & \\ \hline 50^{b} \end{array}$
thiourea)			

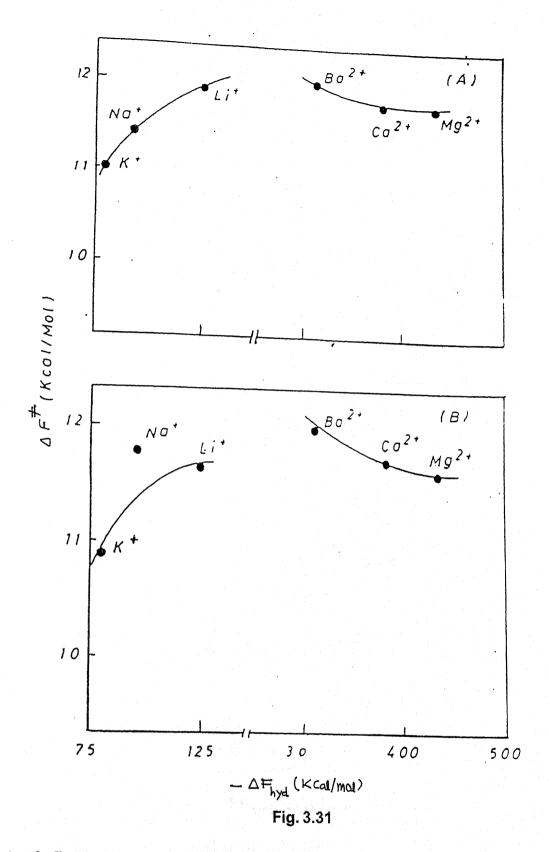
- a. All results correspond to $\lambda = 3 \text{ A}^{\circ}$ unless otherwise noted
- b. Calculations correspond to $\lambda = 1 \text{ A}^{\circ}$
- c. Calculations correspond to $\lambda^2 = 10^{-15} \text{ cm}^2$
- d. Calculations correspond to $\lambda = 5 \text{ A}^{\circ}$

disorder)". On the other hand, Tien and Ting (56) who found negative ΔS^{\pm} values for the permeation of water through very thin (50 A° thickness) bilayer membrane, stressed the possibility that the membrane may not be the rate-determining step. Based on additional experimental data, they came to the conclusion that the solution-membrane interface was the rate-limiting step for permeation.

The results of our investigations (see Tables 3.31 and 3.32) indicate that electrolyte permeation gives rise to negative values for ΔS^{*} . The values of ΔS^{*} for both the membranes show a similar behavior for different electrolytes. It is in general found that as the valance of the individual ion is increased, the decrease in the value of ΔS^{*} is enhanced. Since the membranes used in this study are fairly thick compared to bilayers, it is believed that the membrane along with the solution – membrane interface controlled the electrolyte permeation process. The negative values of ΔS^{*} , therefore, as suggested by Shuller et al. (55) indicate electrolyte permeation with partial immobilization in the membrane, the partial immobility increasing in a relative manner with increase in the valance of the ions constituting the electrolyte.

In Figs. 3.31-3.33 the individual ionic distribution to the property of aqueous ions given by Noyes (57) namely $^{\Delta H}$ hydration, $^{\Delta F}$ Hydration, $^{\Delta S}$ hydration of Li⁺, Na⁺, K⁺ as well as those of Ba²⁺, Ca²⁺ and Mg²⁺ are plotted against the corresponding $^{\Delta H}$, $^{\Delta F}$ and $^{\Delta S}$ values for diffusion through the membranes. It is found that at least some formal relationship exists between these thermodynamic parameters.

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Plots of ΔF* (Kcal/mol) for the diffusion of various electrolytes (At 25°C) against –Δ F_{hyd} (Kcal/mol) for respective cations through polystyrene based (A) cobalt phosphate and (B) nickel phosphate membranes.

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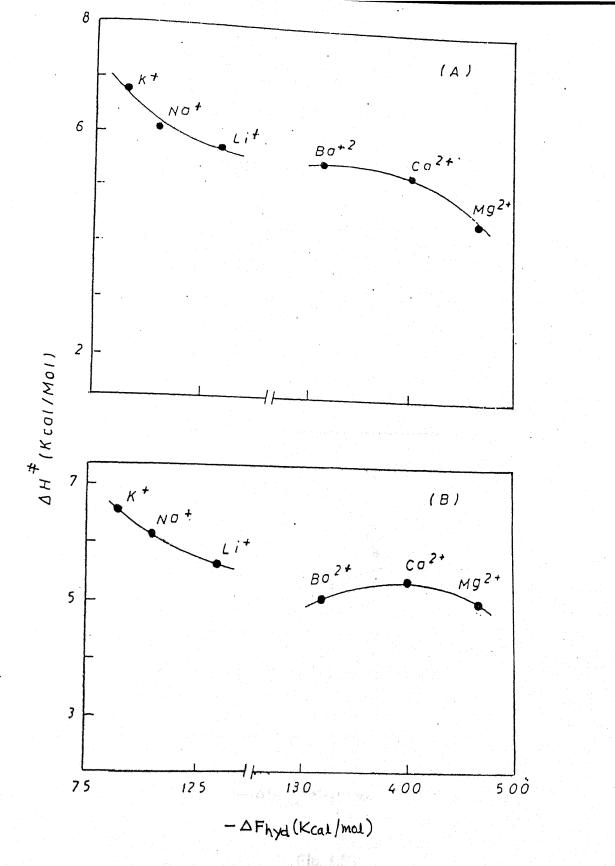


Fig. 3.32

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Plots of ΔH* (Kcal/mol) for the diffusion of various electrolytes (At 25°C) against $-\Delta F_{hyd}(K_{cal}/mol)$ for respective cations through polystyrene based (A) cobalt phosphate and (B) nickel phosphate membranes.

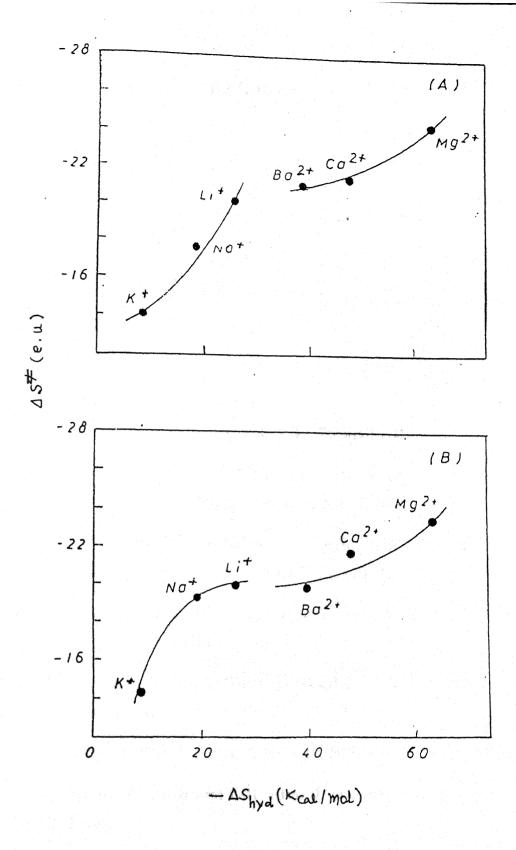


Fig. 3.33

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Plots Δ S* (e.u.) for the diffusion of various electrolytes (at 25°C) against -Δ S_{hyd} (K_{cal}/mol) for respective cations through polystyrene based (A) cobalt phosphate and (B) nickel phosphate membranes.

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SUMMARY

When two solutions of same electrolyte having different concentration are separated by the parchment supported membrane, the mobile species penetrate to membrane phase and various transport phenomena are induced into the system, which has been investigated by taking into account the following aspects:

- (i) Membrane potential
- (ii) Bi-ionic potential
- (iii) Ionic transport
- (iv) Electrical conductivity
- (v) Ionic distribution equilibria, and
- (vi) Spatial distribution of ions and the potential within the membrane.

The classification of the membrane has been carried out time to time by the various investigators. They also defined the membrane in different ways. More over their views have been similar but are not coinciding completely always. However, according to the authors; "A membrane can be regarded as a phase or group of phases that controls the transport of matter and energy between two essentially uniform phases which it separates" is a appropriate description of a membrane which has been described in this thesis thoroughly.

According to the former definition of the membrane based on various aspects, the membranes are classified by taking into account the different aspects, mainly - (i) basis of origin, (ii) basis of nature,

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(iii) basis of physical state, (iv) basis of penetration power and (v) basis of charge etc. The basis of origin is important according to which membrane may be either biological or synthetic. Furthermore, the sub-classification of synthetic membranes is also based on their composition, function, structure and form composition refers to the material used to make the membrane i.e., organic or inorganic polymer. Functional classification includes gas separation, water desalination, dialysis etc. Form denotes whether the membrane is a film, hollow fiber, tube or coating.

The work done using polystyrene based nickel and cobalt phosphate membranes have been described in the thesis under the following three chapters.

Chapter-I has a description of the preparation of new membrane-electrolyte systems of the Polystyrene based nickel and cobalt phosphate membranes. This section deals with the membrane characterization and evaluation of effective fixed charge density of nickel and cobalt phosphate membranes from the membrane potential measurements using various 1:1 electrolytes at different concentrations. The charge densities were evaluated by the following three methods:

- (i) Teorell Meyer and Sievers method.
- (ii) the methods suggested by Kobatake and coworkers.
- (iii) recently developed method of Nagasawa et. al.

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For the measurements of membrane potential across

Polystyrene based nickel and cobalt phosphate membranes chlorides

of K⁺, Na⁺ and Li⁺ were used as electrolyte. The values of membrane potential were found all positive when electrolyte solutions were dilute. It shows that the membranes were cation selective. But when the membranes were used to seperate concentrated electrolyte solutions the values of membrane potential were negative, that is membranes became anion selective. Such reversal in selectivity character is not peculiar to these systems. The values of E_m were found directly proportional to the dilution.

Teorell - Meyer and Sievers (TMS) derived a theoretical equation for membrane potential to evaluate effective fixed charge density of the membrane. The equation was derived when a charged membrane separates different concentrations of an electrolyte by considering a diffusion potential within and two interfacial potentials at the membrane - solution interface. The theoretical values of Em were calculated at various value of u/v. The membrane potential thus derived has been accepted and widely used for the evaluation of fixed charge density and the mobility ratio of the ions within the membranes by plotting method, which gave the satisfactory results. An equation for theoretical membrane potential on the fixed charge concept by utilizying a number of basic assumptions was derived by Kobatake and coworker. Two limiting forms of the equation were derived and used to evaluate the effective fixed charge density of the membranes. In the investigation an interesting point was found to note that the theoretical predictions were borne out quite satisfactorily by our experimental observed results.

Kobatake et. al. also adoped an another method for the membrane potential, similar to the TMS method was used for the

evaluation of effective fixed charge density of the membranes thermodynamically. The equation, derived by Kobatake et.al., starting with the basic flow equation provided by the irreversible thermodynamic processes and using a different set of assumptions. Apparent transference number of coions and permselectivity of the membranes were utilized in this method. In this method permselectivity calculated from apparent transference number was plotted against log (C1+C2)/2, the concentration at which permselectivity becomes 1/5 gave the value of the thermodynamically effective fixed charge density of the membrane.

Recently Nagasawa et. al developed a new method for membrane potential when a charged membrane separates two solution of electrolyte based on irreversible thermodynamic principles. The electrolyte solutions on both the side of membrane were maintained at the same pressure and temperature throughout the experiment. The equation used in this method reduces to a suitable form at sufficiently high electrolyte concentrations which was used in the evaluation of effective fixed charge density of the membrane by plotting method. The values of effective fixed charge densities evaluated from different methods gave identical values.

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The chapter-II of the thesis describes the determination of selectivity of cations on the polystyrene based nickel and cobalt phosphate membranes.

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Initially on the basis of the values of membrane potential observed experimentally across both the Polystyrene based

membranes, selectivity sequence of metal ion was found as:

 $K^+ > Na^+ > Li^+$

theoretical Some equations based on non-equilibrium thermodynamics derived by Kobatake and co-workers for the charged membranes were used to evaluate the effective fixed charge density values of the membrane electrolyte system. Involving the membrane potential measurements in these equations, various thermodynamic membrane parameters were evaluated. Using these values of parameters the effective fixed charge density values against the 1:1 electrolytes of both the membranes are evaluated. The values of apparent transference number t_app and the perm selectivity Ps have been important factors during the electrochemical characterization of the membranes. Another theory developed by Tasaka and co-workers has also been used in the evaluation of magnitude of fixed charge $\emptyset X$. Since the values of ØX thus obtained were quite low, and the membranes were expected to have low electrostatic field strength of the fixed charge sites. For this situation, following the Eisenman and Horn, selectivity sequence of metal ion was proposed.

 $K^+ > Na^+ > Li^+$

Under the heading of bi-ionic method, the values of bi-ionic potential across both the membranes using various combinations of 1:1 electrolytes at different concentrations were measured. The intramembrane permeability ratio values of cations were obtained by the plotting method. Conductivity values of membranes were observed

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experimentally in order to evaluate selectivity of the membranes using the predetermined values of the intramembrane permeability ratio. The sequence of selectivity of metal ion in the membranes phase again was found as:

 $K^+ > Na^+ > Li^+$

which on the basis of the Eisenman-sherry model of membrane selectivity points towards the weak field strength of the charge groups attached to the membrane matrix. Perfect Donnan exclusion of coions was realized in the dilute limit of the external solution.

The mixture method is used to assess the selectivity sequence of the membranes for the cations by evaluating the values of potentiometer selectivity constant K_{ij}^{pot} of the membranes. First of all, the mixture methods were developed and were used extensively by Lengyl and Blum and later by Eisnman, Srinivasan and Rechnitz for the determination of K_{ij}^{pot} Punger and Toth recommended strongly the titration procedure of Dole of the matrix method which was modified and improved by Buck et al, which provided the extensive sets of data for the determination of K_{ij}^{pot} . In this method a set of mixture response potentials were measured by taking fixed concentrations of both the primary ions (i.e. i and j on one side while varying the concentration of ionic species i and j on the other side). The values of K_{ij}^{pot} were derived by using the slope of the lines which were obtained as a curve between electrical potential ΔE_i or ΔE_i and \log_{ai} or \log_{aj} Thus on the basis of K_{ij}^{pot} values the selectivity sequence of metal ions was founds as:

 $K^+ > Na^+ > Li^+$

At last the selectivity sequence of the membranes for the metal ions was also tested in terms of the values of various activation parameters like Ea, ΔF^{\sharp} ΔH^{\sharp} and ΔS^{\sharp} predicted on the basis of rate theory.

The magnitude of ΔS^{\sharp} represents the mechanism of flow and has been interpreted in a number of ways. The negative values of ΔS^{\sharp} , founds for ion permeation are attributed to electrolyte diffusion with partial immobilization in the membrane, the partial immobility increases with the increase of density of charge on the permeant. This conclusion is in good agreement with the most recent findings of Marcus, Who established that the translation immobilization entropy of solvents follows the sequence.

K⁺ > Na⁺ > Li⁺

Chapter-III deals with the preparation of new system of polystyrene based cobalt and nickel phosphate membranes and the studies of diffusion of a number of 1:1, 2:1 and 3:1 type of electrolytes through them. Various membrane parameters, namely, membrane potential E_m , cationic potential $E_{\bar{c}}$ and membrane resistance R_m etc. have been determined with the electrolytes at different concentrations by electrometric method. The diffusion rates were computed using the recently developed equation by Kittleberger based on the simple laws of electrolysis and utilising the derived membrane parameters. The

diffusion rate sequence derived at 25±0.1°C was as follows: K⁺ > Na⁺ > Li⁺ and Mg²+> Ca²+> Ba²+ > A1³+. The diffusion rate sequence of the membranes for various uni, bi and trivalent cations were found to be primarily dependent on the differences in the hydration energies of counterions in the external solution. On the basis of Eisenman-Sherry theory of membrane selectivity this diffusion rate sequence of alkali metal cations point towards the weak field strength of the fixed charge groups on the membrane matrix.

Various membrane transport parameters at different temperatures were also evaluated and the energy of activation Ea for the diffusion of electrolytes were calculated. It was found that the values of Ea for diffusion through the membranes were higher than those found for diffusion in free solution.

The theory of absolute reaction rates was applied for the diffusion process and the various activation parameter namely, enthalpy of activation ΔH^{\sharp} , free energy of activation ΔF^{\sharp} , and entropy of activation ΔS^{\sharp} were evaluated. The values of ΔS^{\sharp} were found to be negative indicating thereby that the diffusion takes place with partial immobilization in the membrane phase. The relative partial immobility was found to increase with increase in the valance of the ion constituting the electrolyte. A formal relationship between $\Delta H_{hydration}$, $\Delta F_{hydration}$ and $\Delta S_{hydration}$ of cations with the corresponding values of ΔH^{\sharp} , ΔF^{\sharp} and ΔS^{\sharp} for diffusion was also found to exist for these membranes.



List of Publications

- 1. Mohd. Ayub Ansari, Manoj Kumar, P. Srivastava, A. Kumar and R.S. Kushwaha, Evaluation of membrane selectivity from electrical potential and conductivity measurements, J. Ind. Council. Chem. Vol. 22, No.2, 23-31 (2005).
- 2. R.S. Kushwaha, Manoj Kumar, B. Rai and Mohd. Ayub Ansari, Transport studies of metal ions through model membrane with the application of absolute reaction rate theory, Proc. Natl. Sem. BRAMUW (2004).
- 3. Mohd. Aybu Ansari and Manoj Kumar, Bi-ionic potential across the inorganic precipitate charged membranes. J. Membrane Science, (Under Communication).
- 4. Manoj Kumar and Mohd Ayub Ansari, Ion transport studies across polystyrene based model membranes, Progressive Research (Under communication).

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Studies of Membrane Selectivity from Electrical Potential and Conductivity Measurements

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The latest theories of membrane ion transport, presented on the basis of non-equilibrium thermodynamics have been applied to potentiometric., measurements for the evaluation of selectivity sequence of metal ions of parchment supported nickel phosphate membrane. Electrical potentials arising across the membrane using various combinations of 1:1 electrolytes at different concentrations have been measured. The conductivity values of the membrane in contact with simple 1:1 electrolytes have also been experimentally observed in order to, evaluate the selectivity of membrane. The selectivity sequence of the membrane was found as:

Which on the basis of the Eisenmen-Sherry model of membrane selectivity, point towards the weak field strength of the charge groups on the membrane matrix perfect Donnan exclusion of coins was realized in the dilute limit of the external solution.

Introduction

When a membrane separates two electrolytes solutions having different concentrations, the mobile species penetrate the membrane and various transport phenomena5 are induced in the system. The total electric potential difference observed under zero current flow between two aqueous solution separated by a membrane has been one of the most widely characterized electrochemical and bioelectric phenomena²⁻⁹. The fixed charge concept of Teorell¹⁰ and Meyer and Sievers¹¹ for the charged membranes is a pertinent starting point of the investigation of actual mechanisms of ionic or molecular processes, which occur in the membrane phase.

The main purpose of the present work is to apply the recently developed non-equilibrium thermodynamic theories to membrane electrical potentials. In order to point out the membrane selectivity of metal ions, membrane conductance in contact with various 1:1 electrolytes has also been observed experimentally to substantiate our findings.

Experimental

Parchment supported membrane of nickel phosphate was prepared by the method of interaction as described earlier⁶. The cell of the following type,

SCE | Electrolyte | Membrane | Electrolyte | SCE | Solution(I) | Solution (II)

was established for measuring the electrical potentials using a pye-precision vernier potentiometer and saturated calomel electrodes (SCE)

The bionic potential developed across the membrane was measured by setting up an electrochemical cell of the following type:

SCE | Solution | Membrane | Solution | SCE | A+M- | II

The values of bi-ionic potential (BIP) of the membrane were measured by taking same concentrations of two different electrolyte A+M-

and B⁺M· type on two sides of the membrane. Aqueous chloride solutions of sodium, potassium and lithium (BDH, AR grade) were used and stirred vigorously with a pair of electrically operated magnetic stirrer to remove completely or at least to minimize the effect of the film controlled diffusion¹².

For the measurement of electrical conductivity, the membrane was first dipped and equilibrated in an appropriate electrolyte solution. It was then clamped between two half-cells and measurements were made, using a conductivity bridge (Cambridge Instructment Co. Ltd., England). All measurements were carried out at $25 \pm 0.1^{\circ}$ C. The error in the measurement of membrane potential was within

± 1% whereas, electrical conductivity could be measured to better than 99.5% accuracy.

Results and Discussion

The values of membrane potential (E_m) observed experimentally across the membrane by taking dilute side positive are depicted in Fig. 1. The Interesting point with the values of (E_m) in fact that these are +ve when the membrane is separating dilute solution of the electrolytes. This means that the membrane is cation selective, and when the membrane is used to separate concentrate solution of the electrolyte, values of Em are -ve, i.e., the membrane becomes anion selective such reversal in selectivity character is not peculiar to phase systems. 15

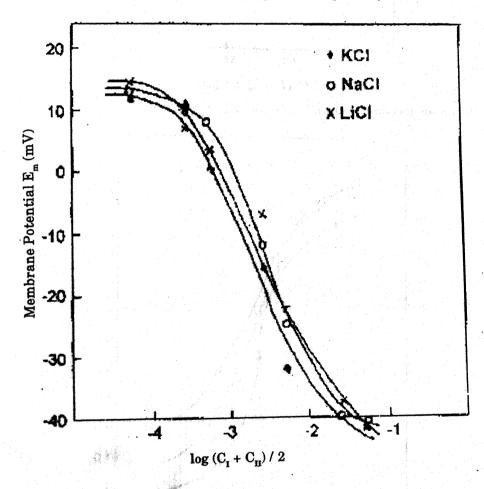


Fig. 1 Plots of membrane potential $E_m(mV)$ against $\log{(C_I + C_{II})}/2$ using 1: 1 electrolytes across nickel phosphate membrane.

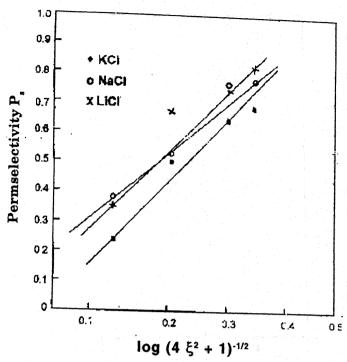


Fig. 2 : Plots of permselectivity P_s vs log $(4 \xi^2 + 1)^{-1/2}$ for nickel phosphate membrane.

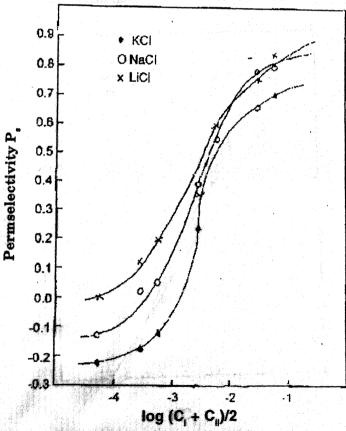


Fig. 3 : Plots of permselectivity P_{μ} vs. log $(C_l + C_{ij})/2$ for nickel phosphate membrane.

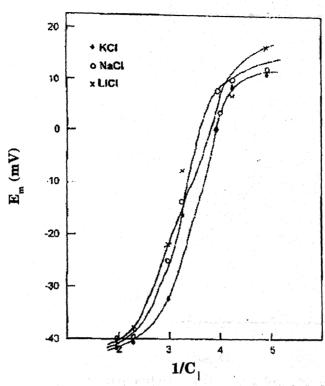


Fig. 4: Plots of Membrane Potential E_m (mV) vs. 1/C₁ for nickel phosphate membrane.

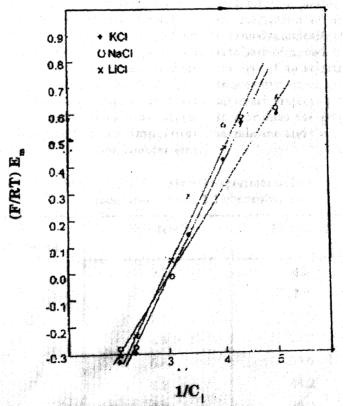


Fig. 5: Plots of (F/RT) E (mV) vs. 1/C for nickel phosphate membrane.

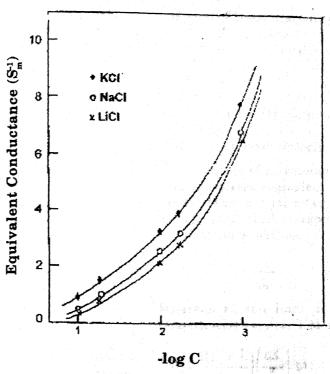


Fig. 6: Typical plots of equivalent coductance (S_m⁻¹) vs. -log C for nickel phosphate membrane.

In the absence or a pressure or temperature gradient, the generation of a electrical membrane potential in presence of two solutions of an electrolyte of different concentrations separated by a membrane, can be attributed to the presence of net charge on the membrane. Such charges play an important role in the sorption and transport of simple electrolytes in artificial as well as natural membranes¹⁴ and impart some important electrochemical properties of co-ions, counter-ions

and neutral molecules. Hence for detailed investigation of membrane selectivity, its thermodynamically effective fixed charge density is to be determined. it can be evaluated by making the use of an equation derived on the basis of thermodynamics of irreversible process. The approach employs a phenomenological coefficient to correlate the gradients that exist across a membrane and their resulting fluxes.

Table 1: Value of bi-ionic (mV) observed experimentally across nickel phosphate membrane using 1:1 electrolyte pair

Electrolyte pair Concentration Mol/I	KCI-NaCl	KCl-LiCl	NaCl-LiCl	
1×10 ⁻¹ /1×10 ⁻¹	0.2	6.1	6.4	
5×10 ⁻² /5×10 ⁻²	1.2	72.	1.8	
2×10 ⁻² /2×10 ⁻²	2.1	10.5	2.7	
1×1 ⁻² /1×10 ⁻²	4.5	13.6	5.1	
5×10 ⁻³ /5×10 ⁻³	5.8	Dr. 1640 to 15.6	6.1	
2×10³/2×10³ 1×10³/1×10³	711 9.2	18.2 20.2	7.7 9.8	

Kobatake and coworkers^{15,16} integrated the basic flow equations, provided by thermodynamics of irreversible processes to derive the following equation for the degree of permselectivity (Ps) of the membrane electrolyte system by taking into consideration and ionizable membrane in contact with solutions of monovalent electrolyte of concentrations $\mathbf{C_1}$ and $\mathbf{C_{11}}$ ($\mathbf{C_{11}} > \mathbf{C_1}$).

$$P_{S} = \frac{I - t_{app} - \alpha}{\alpha - (2\alpha - 1) (l - t_{app})} = \frac{I}{(4\xi^{2} + 1)^{w}}$$
(1)

where α , ξ and t_{app} can be expressed as

$$a = u^{\circ} + u^{\circ}$$
 (2)

$$\xi = C/\phi X \tag{3)(a)}$$

$$t_{app} = (1-\alpha) \frac{4\sqrt{\xi^3+1+1}}{4\sqrt{\xi^3+1(2\alpha+1)}}$$
 (3)(b)

$$E_{m} = -(RT/F) (1-t_{app}) In C_{II}/C_{I}$$
 (4)

The Eqn (1) is used to find the pennselectivity (Ps) from the membrane potential measurement using eqn (4). When the average external salt concentration $C=(C_I+C_{II})/2$ is high in comparison with the thermodynamically effective fixed charge density, ϕX , i.e. $\xi 1 >> 1$, the membrane potential can be expressed as

$$E_{m} = -(RT/F) (2\alpha-1) \operatorname{In} C_{f}/C_{H}$$
 (5)

On the other hand, when the salt concentrations very low, the membrane potential expression becomes.

$$E_{m} = -(RT/F) \text{ In } C_{l}/C_{ll}$$

If the membrane potential is in line with eqn. (6) the membrane may be referred to as a perfectly permselective, where t pecomes zero and Ps tends to unity. On the other hand, when membrane potential follows eqn. (5), t pecomes (1-a) and Ps equal to zero. Hence, it can be said that Ps takes a value between zero and unity depending on the external salt concentration for a given membrane electrolyte system.

In accordance with eqn (1), the straight line plot of Ps against $(4\xi_2 + 1)^{-6}$ (Fig.2) confirms the applicability of this irreversible thermodynamic approach to our model system. When the average concentration, C, and the thermodynamically effective fixed charge density, ϕX , are of the same

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magnitude, ξ becomes equal to unity and Ps equal to $1/\sqrt{5}$. The magnitude of concentration corresponding to this value of Ps is measure of Another expression, which is useful for the evaluation of magnitude of ϕX , has been proposed by Tasaka et al¹⁷. These authors derived an equation for membrane potential taking some assumption into account for low and high concentration limit of electrolyte solutions.

In the absence of an externally applied electric field or a pressure gradient at the limit of low electrolyte concentration (where the effect of flow of water is negligible), the expression for membrane potential can be written.

$$-E_{m} = \frac{RT}{F} \ln \frac{C_{n}}{C_{r}} \tag{7}$$

Whereas at the limit of high electrolyte concentration i.e. near 1 M or more, we have:

$$-E_{m} = \frac{RT}{F} \left(\frac{\gamma - 1}{\gamma}\right) \left(\frac{\phi X}{2}\right) 1/C_{1}$$
 (8)

where r = ratio of electrolyte concentration i.e. $(y = C_{II}/C_{I})$, which predicts a linear relationship between Em and l/q and allows the evaluation of if>X from the slope of straight lines obtained by plotting Em against l/q. if> X has also been related to E_ and t as 18.

$$(F/RT) E_m = -\ln \gamma + \ln \frac{\phi x + \sqrt{(\phi x)^2 + 4C_1^2}}{\phi x + \sqrt{(\phi x)^2 + 4C_1^2}}$$

+(2t_-1) In
$$\left[\frac{(1-2t_-)\phi x + \sqrt{(\phi x)^3 + 4C_{11}^2}}{(1-2t_-)\phi x + \sqrt{(\phi x)^2 + 4C_{12}^2}} \right]$$
(9)

which can be approximated to eqn (10) if the membrane is slightly charged.

$$(F/RT)E_m = (2t_--1)\ln \gamma + \frac{2(\gamma-1)}{\gamma} t(1-t_-) \frac{\phi X}{C_1}$$
 (10)

This equation predicts a straight line plot of (F/RT) Em Versus $1/C_1$ at fixed γ and allows the evaluations of t_- and ϕX from the intercept and slope of the linear plot.

Thus, the equation (1), (8) and (10) have been utilized to calculate the values of ϕX and t_{\perp} (Table 1) by plotting Ps versus $\log (C_1 + C_{11})/2$ (Fig. 3),

 E_m versus $1/C_I$ (Fig. 4) and (F/RT) Em va. $1/C_I$ (Fig. 5). The values of effective fixed charge density, ϕX , thus obtained from the membrane are quite low, which indicate that the membrane has low negative electrostatic field strength of the fixed charge sites. for such a situation following the Eisenman and Horn¹⁹. selectivity sequence of metal ions in the membrane phase was confirmed as,

The selectivity of nickel phosphate membrane for the metal ions can also be satisfied by the most widely used method ofbi-ionic potential.

Selectivity by bi-ionic potential (BIP)

A steady electromotive force of a bi-ionic cell containing two electrolytes A⁺M⁺ and B⁺M-separated by a membrane is called the bi-ionic potential (BIP)²⁰. which is a measure of selectivity of the membrane for ions of the same sign and has been the subject of many theoretical and experimental studies²¹⁻²³. For a general case the bi-ionic potential $\Delta \phi_{BIP}$ for counter ions of equal valencies by Wyllie and Kannan²⁴ is given by the eqn. (11).

$$\Delta \phi_{n\sigma} = \frac{RT}{F} \operatorname{In} a_i \overline{U}_i / a_j \overline{U}_j \tag{11}$$

Where a_ia_j and U_i/U_j are the activity ratio of the solutions and mobility ratio of the ions in the membrane phase respectively. Wyllie²⁴ expressed the inter membrane mobility ratio as:

$$\overline{U_i}\overline{U_j} = \overline{t_i}/\overline{t_j} = \overline{M_i}/\overline{\lambda_i} = \overline{M_j}/\overline{\lambda_i}$$
(12)

Where \bar{t}_i/\bar{t}_j is the intramembrane transference ration and $\overline{M}_i/\overline{M}_j$ are the steady state equilibrium concentration of i and j the respective zones, $\bar{\lambda}_j$ is the conductivity of the membrane when it is wholly i form and $\bar{\lambda}$ is the form conductivity of the membrane when it is wholly in j form. Furthermore, it was shown that $\bar{M}_i/\bar{M}_j \approx K_{ji}$ is the selectivity. This on substitution in eqn. 12 gives.

$$\overline{U}_i/\overline{U}_j = K_{ji}(\overline{\lambda}_i/\overline{\lambda}_j) \tag{13}$$

Thus the ratio of motilities is related to the chemical and electrical properties of the membrane.

The value of bi-ionic potential observed experimentally across the parchment supported nickel phosphate membrane given in Table 1, are used to calculate the intramembrane mobility ratio $\overline{U}_i/\overline{U}_j$ using the eqn. (11). The values thus calculated are given in Table 2. An interesting point with regard to the values of $\overline{U}_i/\overline{U}_j$ is that the mobility ratio undergoes considerable change with the concentration of the each electrolyte pair.

To gain knowledge of selectivity K_{ij} from the predetermined values of $\overline{U}_i/\overline{U}_j$ the ratio of electrical conductivities $\overline{\lambda}_i/\overline{\lambda}_j$ demanded by eqn. (12) must be known. Membrane conductance measurement were carried out when it was wholly

Table 2: Value of the intramembrane mobility ratio f various metal ion pair through the nickel phosphate membrane.

Electrolyte pair Concentration Mol/l	$U_{\rm K}^+$ / $U_{\rm Na}^{+}$	U _K + / U _{Li} +	U _{Na} + / U _{Li} +		
1×10 ⁻¹ /1×10 ⁻¹	0.2	6.1	6.4		
5×10 ⁻² /5×10 ⁻²	1.2	7.2	1.8		
2×10 ⁻² /2×10 ⁻²	2.1	10.5	2.7		
1×10 ⁻² /1×10 ⁻²	4.5	13.6	5.1		
5×10 ⁻³ /5×10 ⁻³	5.8	15.6	6.1		
2×10-3/2×10-3	7.1	18.2	7.7		
1×10 ⁻³ /1×10 ⁻³	9.2	20.2	9.8		

U = mobility of metal ion pair.

in from of i or in from of j. The values of observed membranes conductance shown in fig. 6 where relatively more dependent on the concentration of the electrolytes, which implies that the membrane has a relatively high Donnan uptake and low selectivity constant values. The values of slectivity Kij evaluated using the values of electrical conductivity and the values of intramembrane mobility ratio presenting in Table 2 are given in Table 3. These values of intra-

membrane mobility ratio refer to the same selectivity sequance of the membrane for the cations.

$K^+>Na^+>Li^+$

This order of selectivity on the basis of the Eisenman - Sherry model of membrane selectivity^{25,26} and Kushwaha and co-workers²⁷. point towards the weak field strength of the charge groups attached to the membrane matrix.

Table 3: Value of membrane selectivity constant K_{ji} for various alkali metal ion pairs evaluated from the intra membrane mobility ratio and the ratio of electrical conductance at various electrolyte concentration.

Concentration Membrane M	Nickel Phosphate						
	1×10 ¹ /1×10 ⁻¹	5×10 ⁻² /5×10 ⁻²	2×10 ⁻² /2×10 ⁻²	1×10 ⁻² /1×10 ²	5×10 ⁻³ /5×10 ⁻³	2×10 ⁻³ /2×10 ⁻³	1×10 ⁻³ /1×10 ⁻³
Selectivity Constant							•
K _{NaK}	0.81	0.85	0.98	1.09	0.89	1.15	1.35
K _{LiK}	1.00	1.01	1.03	1.29	1.48	1.26	1.55
K _{LiNa}	1.05	1.10	1.29	0.38	1.56	1.75	1.45

 K_{NaK} : Membrane selectivity Constant for NaCl- KCl pair K_{LiK} : Membrane selectivity Constant for LiCl - KCl pair K_{LiNa} : Membrane selectivity Constant for LiCl - NaCl pair

Acknowledgement

The authors are grateful to Dr. U.P. Singh Principal of the College for providing necessary research facilities.

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